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Occurrence of Pesticides in Drinking Water, Food, and Air
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OCCURRENCE OF PESTICIDES
IN DRINKING WATER, FOOD, AND AIR

Revised Draft Report

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1. ALACHLOR

1.1 GENERAL CHARACTERISTICS

1.1.1 Physical/Chemical Properties

Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl acetanilide)] is a pre-emergent amide herbicide. Synonyms and identifiers for alachlor are Alanex, Alanox, and Lasso® (Berg 1986; SRI 1983). Alachlor is often applied as a mixture with atrazine; this product is also known as Alazine (Berg 1986).

Alachlor is a white crystalline solid at 25°C (USEPA 1984d). It has a molecular weight of 269.8, a molecular formula of $C_{14}H_{20}NO_2Cl$, and a melting point of 39.5 to 41.5°C (USEPA 1984; Berg 1986). The aqueous solubility and vapor pressure of alachlor at 25°C are 242 mg/l (8.97×10^{-4} mol/l) and 2.2×10^{-5} torr (2.89×10^{-8} atm), respectively (Cohen et al. 1984).

Based on the reported vapor pressure and aqueous solubility, Henry's constant for alachlor at 25°C is estimated to be 3.2×10^{-8} atm·m³/mol. Kenaga and Goring (1978) report a K_{OC} value of 190 for alachlor.

1.1.2 Use

Alachlor is a herbicide recommended for control of yellow nut sedge, annual grasses, and broadleaf weeds. The product can be applied either as a surface application after planting or shallowly incorporated before planting in the upper 1 to 2 inches of soil. The recommended rate of application is 2.5 to 4 quarts per acre (CPCR 1986). Total U.S. alachlor usage ranges between 80 and 85 million pounds of active ingredient annually (Kuch 1986).

Nearly all (96 to 98%) of the domestically supplied alachlor is applied to field corn and soybeans (Glaze 1982). The major field corn producing states are located in the Corn Belt (Illinois, Indiana, Iowa, Kentucky, Missouri, Ohio); the Northern Plains (Kansas, Nebraska, North Dakota); the Lake States (Michigan, Minnesota, Wisconsin); and the Southeast (Georgia, North Carolina). Pennsylvania and Texas are also considered major field corn

producing states. Approximately 52 million pounds of alachlor active ingredient were used on field corn in these states and regions in 1982 (USDA 1983).

Approximately 33 million pounds of alachlor active ingredient were used on soybeans in the major soybean producing states in 1980. These states are located in the North Central region (Illinois, Indiana, Iowa, Kansas, Minnesota, Nebraska, Ohio); the Mississippi Valley (Arkansas, Kentucky, Louisiana, Mississippi, Tennessee); and the Southeast (Alabama, Georgia, North Carolina, South Carolina) (Hanthorn et al. 1982). Florida also reported the use of alachlor on soybeans (Lipsey 1981).

The remaining 2 to 4 percent of alachlor production is used on other crops, including: peanuts, potatoes, ornamentals, grain sorghum, dry edible beans, cotton, tobacco, sugar cane, and strawberries (Glaze 1982, USDA 1983, Lipsey 1981, Parks 1983). Some of these uses are restricted by location (USEPA 1982a).

1.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of alachlor is divided into the following subsections: 1.1.3.1 Volatilization; 1.1.3.2 Sorption and Leaching Potential; 1.1.3.3 Abiotic Transformations; 1.1.3.4 Biodegradation; 1.1.3.5 Fate in Water Treatment Plants; and 1.1.3.6 Summary. The discussion will emphasize the environmental fate of alachlor in soil and water.

1.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as alachlor ($H = 3.2 \times 10^{-8} \text{ atm}\cdot\text{m}^3/\text{mol}$) with Henry's constants less than $3.0 \times 10^{-7} \text{ atm}\cdot\text{m}^3/\text{mol}$ are unlikely to undergo significant rates of volatilization from natural waters under any conditions normally found in the environment. Volatilization half-lives estimated by SAIC (see Appendix A) for alachlor in shallow water under turbulent conditions support that conclusion. The estimated volatilization half-lives for alachlor in a turbulent lake 1 m deep and in a stream 1 m deep with a mean current of 2 m/s and exposed to a mean wind velocity of 5 m/s are 7.9 years and 2.9 years, respectively.

Volatilization rates of alachlor from groundwater to the soil column above are projected to be substantially less than volatilization rates from surface waters to the atmosphere. This is due primarily to the laminar, nonturbulent nature of groundwater flow. Transport from groundwater by volatilization may be further reduced by a build-up of chemicals in the pore air at the pore air/groundwater interface, and an associated decrease in the concentration gradient across the interface.

SAIC estimated a volatilization half-life for alachlor applied to the soil surface of only 33 days (see Appendix A). That suggests that volatilization could be substantially involved in the removal of alachlor from surface soils. This conclusion is supported by the experimental results published by Hargrove and Merkle (1971) and Beestman and Deming (1974, as cited in USEPA 1984d. They reported that substantial losses of alachlor from moist silt and sandy loam soils occurred through volatilization (USEPA 1984d).

The relatively short estimated volatilization half-life for alachlor from the soil surface compared to that for volatilization from water is due to the relatively small reported value of the organic carbon normalized sediment or soil/water equilibrium partition coefficient ($K_{OC} = 190$). Volatilization rates for alachlor below the surface of the soil would probably be much slower than at the soil surface.

1.1.3.2 Sorption and Leaching Potential

Based on the reported K_{OC} value of 190 for alachlor, the estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) range from 1.9 to 15 (see Appendix A). As discussed in Appendix A, the $K_{S/W}$ values would probably have to exceed 100 in most aquatic systems for the ratio of the chemical mass adsorbed to suspended and exposed bottom sediment to the chemical mass dissolved in the water column to exceed 0.1. The reason is that in most aquatic systems most of the time, the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 10^3 (USGS 1983). Therefore, transport by adsorption to suspended sediments and removal by adsorption to bottom sediments are probably generally not very important processes for alachlor in most aquatic systems.

Based on its K_{oc} value, alachlor would be classified as moderately resistant to leaching from surface soils using five mobility classes defined by Helling and Turner (1968 and cited in Hamaker 1975). The results of various monitoring studies have supported that conclusion by showing that most of the alachlor remains in the top 0-5 cm or 0-10 cm of soil layers and that surface runoff does not generally remove substantial amounts of alachlor from soil (USEPA 1984d). However, low levels (e.g., .04 ug/l) of alachlor have been detected in 2 out of 14 wells sampled in a corn growing area of Nebraska with sandy soils and shallow unconfined aquifers (Cohen et al. 1984). Also, Wauchope (1978) reported that 3 to 14 percent of applied alachlor was lost to surface runoff during a catastrophic flood (greater than 100-year frequency).

1.1.3.3 Abiotic Transformations

No information was found on the hydrolysis of alachlor in the literature reviewed by USEPA (1984d) or SAIC. Alachlor is apparently susceptible to some form of photodecomposition in water with a surfactant present and on soil (Fang 1977 and Tanaka et al. 1981, as cited in USEPA 1984d). Tanaka et al. (1981, as cited in USEPA 1984d) reported that alachlor in solution at an initial concentration of 100 ppm was 85 percent degraded in the presence of a surfactant after 138 minutes exposure to 300 nm UV light. In the absence of the surfactant, only 1 percent was degraded. Therefore, most of the photodecomposition does not appear to be due to direct photolysis.

1.1.3.4 Biodegradation and Persistence in Soil

Biodegradation appears to be the primary mechanism of removal for alachlor in soil. The reported half-life for alachlor in a laboratory incubated silt soil was 8 days compared to 470 days in an autoclaved soil (Beestman and Deming 1974, as cited in USEPA 1984d). Reported half-lives for alachlor in soils under laboratory and field conditions have ranged from 4 days to 10 weeks (Cohen et al. 1984; USEPA 1984d). Therefore, it would be classified as nonpersistent (half-life <20 days) to moderately persistent (20 days $\leq$ half-life $\leq$ 100 days) by Rao and Davidson (1980). The persistence of alachlor in sandy soils and in soils with low organic content appears generally to be less than in other soils (USEPA 1982a). A half-life of 14 days has been reported for alachlor in anaerobic stream sediments (USEPA 1980c).

1.1.3.5 Fate in Water Treatment Plants

Baker et al. (1981), as cited in USEPA 1985a), reported that a conventional water treatment process consisting of alum coagulation, flocculation, sedimentation, and filtration was generally less than 50 percent effective in removing alachlor from influents at initial concentrations of <0.2 to 2.0 ug/l . In addition, activated carbon adsorption may not be efficient due to low reported break-through volumes for alachlor (De Filippi et al. 1980, as cited in USEPA 1985a). Studies of levels of alachlor in raw and treated surface water confirm that conventional treatment practices are not effective in removing alachlor (Monsanto 1986).

1.1.3.6 Summary

Based on the above discussion and the literature reviews by Cohen et al. (1984) and USEPA (1984d), the following conclusions can be made concerning the most likely behavior of alachlor in soil and water:

- o Biodegradation appears to be the primary mechanism for removal of alachlor from soils. Reported half-lives for soil range from 4 days to 10 weeks.
- o Alachlor is unlikely to undergo significant rates of volatilization from surface water or groundwater under any conditions normally found in the environment.
- o Volatilization appears to be a significant removal process for alachlor on the soil surface. SAIC estimated a volatilization half-life of 33 days for alachlor on the soil surface.
- o Alachlor is expected to remain in solution in surface waters and not bind to suspended solids. This is consistent with the findings that alachlor is not removed by conventional drinking water treatment practices such as filtration.
- o Based on both theoretical and experimental results, alachlor can be classified as at least moderately resistant to leaching from soils.
- o No information was available on the hydrolysis of alachlor. Alachlor appears to be susceptible to some form of photodecomposition in the environment, but not to direct photolysis.
- o Due to its moderate immobility, moderate resistance to leaching, and low to moderate persistence in soils, alachlor is unlikely to significantly contaminate large numbers of surface water or groundwater supplies. However, some limited contamination of shallow unconfined aquifers or streams located near areas of alachlor use may occur.

- o Due to alachlor's low volatility and high solubility, it has considerable potential for the contamination of surface water.

1.2 OCCURRENCE IN THE ENVIRONMENT

1.2.1 Water

This section presents available data for monitoring studies and surveys to determine the extent of occurrence of alachlor in public drinking water supplies and water other than drinking water.

1.2.1.1 Occurrence in Drinking Water

A number of studies provided data on the occurrence of alachlor in public drinking water supplies. These studies, which were conducted on both regional and national scales, are summarized in the following section.

Groundwater Sources -- National Study

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) was conducted by SRI from June 1977 to March 1981. Samples of finished drinking water were collected from 12 groundwater systems of varying size throughout the United States and analyzed for alachlor. None of the drinking water samples from the 12 groundwater systems contained levels of alachlor in excess of the quantification limit of 0.1 ug/l.

Groundwater Sources -- Regional Studies

Drinking water wells from eight counties in Maryland were examined by the State of Maryland's Office of Environmental Programs, Department of Health and Mental Hygiene, in the fall of 1983 (State of Maryland 1983). Thirteen samples were collected from 11 locations and analyzed for alachlor. Two samples were positive at concentrations of 0.1 and 0.8 ug/l. The detection limit was 0.1 ug/l.

The Suffolk County Department of Health Services analyzed drinking water wells in Long Island, New York, during 1984 (Holden 1986). Alachlor was not detected in any of 24 samples collected (detection limit not reported).

Drinking water wells throughout the State of Wisconsin were analyzed by Union Carbide during 1983-1984 as part of a program by the Wisconsin DNR (Holden 1986). Possible contamination may have occurred from both point and nonpoint sources. Of the 377 samples analyzed, 47 were found positive for alachlor with a maximum concentration of 88 ug/l. The mean concentration, range of values, and detection limit were not reported.

Two studies of drinking water wells in Iowa were available for information on the occurrence of alachlor; one conducted by the Iowa State University and the other by the Iowa Department of Water, Air, and Waste Management (Baker and Austin 1983; Kelley and Wnuk 1986). Combined, the studies included six Iowa counties sampled between 1981 and 1985. Fifty-nine samples were analyzed from 25 sites, with all but one positive sample coming from Humboldt County. The overall range was 0 to 2.7 ug/l (the detection limit for this high value was 0.01 ug/l). The one positive sample from outside Humboldt County was 0.18 ug/l. The mean for Humboldt County samples, all taken at one site, was 0.08 ug/l (the detection limit was 0.01 ug/l). The total number of positives and other detection limits were not reported.

Surface Water Sources -- National Study

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) also contained information on alachlor contamination in drinking water from surface water sources. Finished drinking water samples, collected from 104 surface water systems of varying size throughout the United States, were analyzed for alachlor. Drinking water samples from four very large systems (serving greater than 100,000 individuals), were found to contain levels of alachlor in excess of the quantification limit of 0.1 ug/l, ranging between 0.1 and 0.9 ug/l, with an average value of 0.38 ug/l.

Surface Water Sources -- Regional Studies

Alachlor was monitored for in known high-use areas of Illinois, Indiana, Iowa, Michigan, Missouri, North Carolina, and Ohio (Monsanto 1986). Sampling occurred at 24 community water treatment plants in these seven states, which primarily or exclusively utilize surface water supplies. Populations of the

24 communities ranged from 356 to 388,000 and, overall, the study is representative of over 1.3 million people using public drinking water. Both raw and finished water samples were collected daily from each location for 1 year, and were turned into weekly composites (as are presented in the report). Sampling took place between April 1985 and April 1986. The lower limit of method validation (LLMV) was 0.02 ug/l.

Alachlor was not detected in any weekly sample of finished water from 10 of the 24 plants. Of the other 14 plants, the annualized mean concentration (AMC - i.e., a time-weighted average concentration) at 12 plants was less than 0.50 ug/l. The other two plants had AMCs of 0.69 ug/l and 1.4 ug/l. Rarely was alachlor found above 2.0 ug/l in a weekly composite; only 2.6 percent of the weekly composites exceeded 2.0 ug/l during the sampling year (Monsanto 1986). The weekly composite maximum concentrations ranged from <0.20 to 10.7 ug/l for raw water samples and from <0.20 to 10.9 ug/l for finished water samples. The AMCs ranged from 0 to 1.5 ug/l for raw water samples, and from 0 to 1.4 ug/l for finished water samples. [Note: For the AMC range, the lower value assumes that all non-detected = 0 ug/l and the higher value assumes that all non-detected = 0.20 ug/l.] Individual sample results were not presented in the report.

Baker (1983) provided the results of analysis of finished drinking water samples collected from a water supply in Ohio from 1981-1982. The supply obtained water from a river draining an agricultural area. Between June 1981 and July 1982, 15 finished drinking water samples were collected from this plant. Although no detection limits were given, 14 of the samples had positive concentrations of alachlor that ranged between 0.03 and 14.3 ug/l, with an average of 4.5 ug/l.

In another study by Baker (1983), 49 samples were collected from 3 water supplies in Ohio and analyzed for alachlor. The supplies obtained their raw water from two rivers that drain agricultural areas. Average concentrations for samples collected at each of the supplies between May 28 and July 27, 1983 were 1.08 (18 samples), 0.22 (15 samples), and 1.87 ug/l (16 samples). Peak concentrations observed in 1983 were 2.73, 0.47, and 5.91 ug/l, respectively. Datta (no date) reported an overall mean concentration of 1.07 ug/l

for these supplies. The detection limit and number of positive samples were not reported.

Finished drinking water samples from New Orleans, Louisiana were analyzed by Keith et al. (1976, as cited in USEPA 1984d). The range of positive samples for alachlor was 0.17 to 2.9 ug/l. The number of samples analyzed, number of positive samples, mean, and detection limit were not reported.

1.2.1.2 Occurrence in Water Other Than Drinking Water

Eleven studies provided data on concentrations of alachlor in water other than drinking water. Three studies assessed levels of alachlor in groundwater, and eight studies provided information on levels of alachlor in surface water other than drinking water.

Ground Water Sources

Spalding et al. (1980, as cited in Cohen et al. 1984) presented data from a study conducted in atrazine high-use areas of Nebraska. Water samples from 14 wells, out of a total of more than 1,000 wells that were studied in the area, were selected as representative of water in the area. Water samples from 2 of the 14 wells contained an average alachlor concentration of approximately 0.04 ug/l (range = 0.018 to 0.071 ug/l). No detection limit was reported.

In addition, ground water wells from Nebraska, as well as from Iowa, Maryland, and Pennsylvania, have been found to have concentrations of alachlor typically in the range of 0.1 to 10.0 ug/l (Cohen et al. 1986). No other information on these wells was available.

Ground water wells and spring water in the Big Spring Basin, Clayton County, Iowa, were sampled during 1981-1982 for the occurrence of alachlor (Datta no date). Ninety-five samples from 21 locations were analyzed for alachlor, and 4 positive samples were found. An overall mean of 0.082 ug/l (range = 0.05 to 0.15 ug/l) was calculated.

A survey of alachlor in rural private wells was performed (Monsanto 1986). The survey analyzed for alachlor in 246 wells in 9 states. The wells sampled were selected from private wells in areas where alachlor was extensively used. Of the 246 wells sampled, 10 wells had detectable levels of alachlor. The highest level reported was 5.8 ug/l. The remaining nine wells had levels below 1 ug/l. The detection limit was 0.1 ug/l.

Surface Water Sources

Baker et al. (1981) presented data from a study that examined concentrations of alachlor in streamwater in Ohio. A total of 292 samples were collected from 12 different streams during the spring and summer of 1981, and analyzed for alachlor. The analysis identified 235 (80%) positive samples. The maximum concentration observed was 104.6 ug/l. No detection limit for the analysis was given.

Baker (1983) reported on levels of alachlor in water samples collected from two Ohio rivers. Between May 28, 1983 and July 27, 1983, a total of 46 samples was collected (23 samples from each river). The average alachlor concentrations for samples collected and analyzed from each of the rivers was 1.24 ug/l and 3.11 ug/l, respectively. The number of positive values and the detection limit for alachlor were not reported.

Another study examining surface waters in Ohio was reviewed for alachlor occurrence data. Datta (no date) reported analyses of a creek in southwest Ohio during 1981, and again in 1982. Mean concentrations of alachlor for the two years were 13.9 ug/l and 7.6 ug/l, respectively. No other information was reported. The same source (Datta no date) also reported that for 5 northwest Ohio rivers, 233 samples were found to have a mean of peak concentrations of 23.2 ug/l (maximum concentration = 69.6 ug/l). The number of positives and detection limit were not reported.

River samples from the Little Sioux River in northwest Iowa and Big Spring Basin, Iowa, were analyzed for alachlor by the Iowa Department of Water, Air, and Waste Management and as part of the Review of Hydrogeology, Water Quality, and Land Management in the Big Spring Basin, respectively

(Kelly and Wnuk 1986; Datta no date). During the overall study period from 1981 to 1985, 18 samples from 5 locations were taken and 10 proved positive for alachlor. These positive samples represent a mean of 2.59 ug/l (range = 0.06-20.0 ug/l). No detection limit was given. A reservoir on the Des Moines River was sampled for alachlor during 1977-1978 by Leung et al. (1982, as cited in USEPA 1984d). Three sites were sampled (upstream, within, and downstream of the reservoir). A mean concentration of 0.089 ug/l (range = 0 to 0.82 ug/l) was reported for positive samples. The number of positives, number of samples, and detection limit were not reported.

Twenty-five samples from River Raisin, Michigan, were taken at U.S. Geological Survey stations during 1982 (Datta no date). A maximum concentration of 8.16 ug/l was reported for alachlor. No other information was reported.

Dudley and Karr (1980, as cited in USEPA 1984d) analyzed levels of atrazine and alachlor in 45 samples of water, sediment, and fish. The samples were collected in mid-July from a stream draining an agricultural watershed (Black Creek) in Allen County, Indiana. No samples of water showed levels of alachlor in excess of the detection limit of 100 ug/l. The exact number of water samples was not reported.

Schepers et al. (1980, as cited in Baker et al. 1981) assessed concentrations of alachlor in 30 samples of water collected from a watershed in Nebraska. Concentrations of alachlor in the 30 samples ranged between "non-detectable" and 1.41 ug/l. However, the period of collection, detection limit, and number of positive samples for alachlor were not reported.

Lake Erie water samples were collected during a study by Konasewich et al. (1978, as cited in USEPA 1984d). Three samples were positive for alachlor at a mean concentration of 3.05 ug/l (range = 0.07-9.0 ug/l). The number of samples and detection limit were not reported.

1.2.2 Occurrence in Ambient Air

No information was found on concentrations of alachlor in ambient air. Based on alachlor's relatively low vapor pressure and widely dispersed releases from agricultural application, alachlor is not expected to occur in air at significant levels.

1.2.3 Soil/Sediments

Two studies were identified that reported alachlor levels in sediments. There were no studies identified that examined alachlor levels in soils. Dudley and Karr (1980 as cited in USEPA 1984d) analyzed levels of alachlor in 45 sediment samples, of which none were found to contain levels above the detection limit of 100 ug/l (ppb).

Baker et al. (1979, as cited in USEPA 1984d) reported that 6 weeks after alachlor was applied (2.4 kg/ha) to an Iowa watershed, 1.0 ppm of its residues were found in sediment from surface runoff events.

1.2.4 Food

Very little information was available on the occurrence of alachlor in food in the United States. Three studies were identified; however, their resulting data were limited. Hunt et al. (1980, as cited in USEPA 1984d) reported that cabbage grown in soil sprayed with alachlor at the rate of 3.4 kg/ha and 6.8 kg/ha had no detectable residues when harvested 6 weeks later.

Brookhart and Johnson (1977) analyzed fish tissue from fish caught in nine rivers that empty into the Chesapeake Bay. All samples contained less than 0.1 ug/g alachlor. Lastly, Dudley and Karr (1980, as cited in USEPA 1984d) reported no detectable alachlor in fish in the Black Creek watershed in Allen County, Indiana, in 1977. In conclusion, because the information obtained during these studies is not representative of most food groups that constitute an average diet, it was impossible to calculate the typical dietary intake.

1.3 EXPOSURE SUMMARY

Limited studies have been conducted that provide useful data on the extent of occurrence of alachlor in drinking water, food, and air. National monitoring surveys of public water supplies from both ground and surface water sources have reported alachlor levels to be <1.0 ug/l. Regional studies of surface water sources from areas of high alachlor usage have reported levels greater than 10 ug/l. However, typical concentrations tend to be much lower. No data are available on alachlor levels in food or ambient air.

The available data on alachlor in drinking water are insufficient to determine national exposure levels. However, based on a concentration of 10 ug/l, daily intake would be 20 ug/day. Alachlor concentrations in food and air are unknown. Consequently, it is not possible to determine the total exposure to alachlor or to determine which of the three sources of exposure is the major contributor to total daily intake.

2. ALDICARB

2.0 SUMMARY

Aldicarb is a widely used insecticide. Both aldicarb and its degradation products are relatively stable and mobile in groundwater. Data are not available to characterize levels of aldicarb in drinking water. Low levels of aldicarb have been reported in wells near its use.

2.1 GENERAL CHARACTERISTICS

2.1.1 Physical/Chemical Properties

Aldicarb [2-methyl-2(methylthio)propionaldehyde-o-(methylcarbamoyl)oxime] is a carbamate pesticide, a synthetic relative of the alkaloid physostigmine. It is a systemic insecticide, acaricide, and nematicide. Synonyms for aldicarb are Temik, OMS 771, and UC21149 (Berg 1986).

Aldicarb is a white crystalline solid at 25°C (Verschuere 1983). It has a molecular weight of 190.25, a molecular formula of $C_{17}H_{14}N_2O_2S$, and a melting point of 99 to 100°C (Windholz 1976). The aqueous solubility and vapor pressure of aldicarb at 25°C are 6.0 g/l (3.2×10^{-2} mol/l) and 1.0×10^{-4} torr (1.3×10^{-7} atm), respectively (Verschuere 1983).

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant at 25°C for aldicarb of 4.06×10^{-9} atm·m³/mol. Rao and Davidson (1980) report an octanol/water partition coefficient (K_{ow}) of 5 for aldicarb. Aldicarb has an estimated organic carbon normalized soil/water equilibrium coefficient (K_{oc}) of 36 (Cohen et al. 1984).

Under aerobic conditions in aqueous solution, aldicarb is rapidly transformed to aldicarb sulfone and aldicarb sulfoxide, which have aqueous solubilities of 7.8 and 43 g/l, respectively (Cohen et al. 1984).

2.1.2 Use

Aldicarb is registered as a restricted use insecticide/nematicide in 10 or 15 percent granular formulations (Berg 1986). Registered uses of aldicarb include cotton, potatoes, peanuts, soybeans, pecans, sugar beets, citrus fruit, sweet potatoes, edible beans, sugarcane, sorghum, and ornamentals (commercial field grown and nursery plantings, greenhouse crops, and potted plants) (Holtorf 1982).

EPA estimated that domestic usage of aldicarb ranged from 5 to 6 million pounds annually as of 1986 (Kuch 1986). In 1982, approximately 54 percent of annual domestic usage was applied to cotton and potatoes. Other major uses of aldicarb include application to peanuts, soybeans, and pecans which, combined with usage on cotton and potatoes, constitute 90 percent of the estimated annual domestic usage (Holtorf 1982).

A number of restrictions govern the use of aldicarb, including site, volume, and insect specific restrictions, and guidelines for methods of application. Since 1979, registrations and label restrictions have prohibited any aldicarb use on Long Island, New York, after the discovery of aldicarb in groundwater in that area resulted in the closing of several wells (USEPA 1983a).^{*} In 1983, Florida suspended the use of aldicarb on citrus fruits; that suspension is still in effect. Wisconsin and Maine restricted application to potatoes to emergence stage only. Fifteen counties, from Massachusetts to Virginia, have similar label restrictions prohibiting use on potatoes (CPCR 1986).

For most agricultural crops, use of aldicarb is restricted to one application per crop. For cotton and sugar beets, aldicarb use is restricted to two and three applications per crop, respectively (USEPA 1982b). Aldicarb granules are applied in 4 to 6 inch bands over a row on top of the hill. They

^{*}Personal communication between Dennis Edwards, Office of Pesticide Programs, U.S. Environmental Protection Agency, Washington, DC, and Chris Rioux, SAIC JRB Associates), May 1984.

can also be drilled into the soil or planted with the seed (CPCR 1986). Working the product into the soil to 2 to 4 inches is recommended.

Restrictions on volume of application have also been defined for aldicarb and range from 2 pounds per acre for the treatment of aphids on dried-type beans to 67 pounds per acre for the treatment of aphids and mites on pecans. The average application rate for nematodes is 14 pounds per acre; leafhoppers average 7-14 pounds per acre (CPCR 1986).

2.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of aldicarb, aldicarb sulfoxide, and aldicarb sulfone is divided into the following subsections: 2.1.3.1 Volatilization; 2.1.3.2 Sorption and Leaching Potential; 2.1.3.3 Abiotic Transformations; 2.1.3.4 Biodegradation and Persistence in Soil and Water; and 2.1.3.5 Summary. The discussion will emphasize the environmental fate of aldicarb and to a much lesser extent aldicarb sulfoxide and aldicarb sulfone in soil and water. Aldicarb sulfoxide and aldicarb sulfone are products of aldicarb degradation in water and soil under aerobic conditions.

2.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as aldicarb ($H = 4.1 \times 10^{-9} \text{ atm}\cdot\text{m}^3/\text{mol}$) with Henry's constants less than $3.0 \times 10^{-7} \text{ atm}\cdot\text{m}^3/\text{mol}$ are unlikely to undergo significant rates of volatilization from natural waters under any conditions normally found in the environment. The volatilization half-lives SAIC estimated for aldicarb in shallow waters under turbulent conditions using equations A-1 and A-3 through A-8 support that conclusion. The estimated volatilization half-lives for aldicarb in a turbulent lake 1 m deep and in a shallow turbulent river or stream 1 m deep are 51 years and 19 years, respectively (see Appendix A).

By substituting the reported K_{OC} value for aldicarb of 36 into equation A-9 along with the compound's vapor pressure ($1.0 \times 10^{-4} \text{ torr}$) and aqueous solubility ($6.0 \times 10^3 \text{ mg/l}$), SAIC estimates a volatilization half-life for aldicarb on soil of 34 days. Therefore, volatilization may be an important

removal process for aldicarb on the soil surface, depending on the rates of other removal processes. Although volatilization rates of aldicarb beneath the soil surface would probably be much slower, decreasing rapidly with increasing soil depth, Bromilow et al. (1980, as cited in Cohen et al. 1984) suggested that volatilization could substantially contribute to the loss of aldicarb from soil.

No information was found concerning the vapor pressures or volatilization rates of aldicarb sulfone and sulfoxide.

2.1.3.2 Sorption and Leaching Potential

Substituting the estimated K_{OC} value of 36 into equation A-11 gives estimated sediment or soil/water partition coefficients ($K_{S/W}$) for aldicarb ranging from 0.36 to 2.9 for sediments or soils with organic carbon fractions ranging from 0.01 to 0.08, respectively. Aldicarb sulfoxide has reported $K_{S/W}$ values of 0.34 and 3.3 for soils with an organic fraction of 0.14 (Cohen et al. 1984). Since $K_{S/W}$ values for both aldicarb and aldicarb sulfoxide appear to generally be less than 10, it is unlikely that the ratio of the total mass of aldicarb residues adsorbed to suspended and exposed bottom sediment to the total mass of aldicarb residues dissolved in the water column will exceed 0.01 in most surface waters. The reason, as discussed in Appendix A, is that the ratio of the water mass to the suspended and exposed bottom sediment mass exceed 10^3 in most surface waters (USGS 1983). Therefore, it is unlikely that transport by adsorption to suspended sediment and removal by adsorption to exposed bottom sediments are important processes for either aldicarb or aldicarb sulfoxide in surface waters.

Substitution of the estimated K_{OC} value of 36 into equation A-13 gives an estimated soil TLC R_f value (see Appendix A) of 0.71 for aldicarb adsorbed to a soil with an organic fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling and Turner (1968 and cited in Hamaker 1975) for a soil with the same properties (Appendix A), aldicarb would be expected to be moderately mobile (Class 4) in, and be moderately susceptible to leaching from, surface soil. Since reported $K_{S/W}$ values for aldicarb sulfoxide are similar to those

from aldicarb, and since the aqueous solubility of aldicarb sulfoxide (43 g/l) is several times greater than aldicarb, it would be expected that aldicarb sulfoxide would be more susceptible to leaching than aldicarb. The susceptibility of not only aldicarb and aldicarb sulfoxide, but also aldicarb sulfone to leaching from soil, is demonstrated by reported aldicarb residues typically ranging from 1 to 50 ppb in numerous groundwater samples taken from several states (Cohen et al. 1984).

2.1.3.3 Abiotic Transformations

Aldicarb has reported hydrolysis half-lives of 12.5 years at pH 5.5 and 50°C, 5 years at pH 7.5 and 150°C, and 3.5 years at pH 8.5 and 50°C (Hansen and Spiegel 1983, as cited in Cohen et al. 1984). Aldicarb sulfoxide has reported hydrolysis half-lives in groundwater at 150°C of 22 years at pH 6, 2.2 years at pH 7, 82 days at pH 8, and 8.2 days (by extrapolation) at pH 9 (Lemley and Zhong 1984). Aldicarb sulfone has reported hydrolysis half-lives in groundwater at 150°C of 6.7 years at pH 6, 243 days at pH 7, 24.3 days at pH 8, and 2.4 days (by extrapolation) at pH 9 (Lemley and Zhong 1984). Based on these results, it appears that hydrolysis would not be an important removal process for aldicarb over the normal pH range of 6 to 9 in natural waters or for aldicarb sulfoxide and aldicarb sulfone at pHs less than 8. However, at pHs greater than 8, hydrolysis may become an important removal process for aldicarb sulfoxide and aldicarb sulfone.

No information was available in the literature reviewed by Cohen et al. (1984) or SAIC concerning the photolysis or photo-oxidation of any of the aldicarb compounds.

2.1.3.4 Biodegradation and Persistence in Soil and Water

Under aerobic conditions, oxidative half-lives for the oxidation of aldicarb to aldicarb sulfoxide and aldicarb sulfone in soil and water are reported to generally be less than 2 weeks (Bromilow et al. 1980, as cited in Cohen et al. 1984). Under anaerobic conditions, aldicarb sulfoxide and aldicarb sulfone are susceptible to reduction to aldicarb sulfide (Cohen et al. 1984). Therefore, aldicarb in aerobic soils and possibly aldicarb

sulfoxide and aldicarb sulfone in anaerobic soils could be classified as nonpersistent (half-lives <20 days) in soils by Rao and Davidson (1980). There was no information available on the persistence of aldicarb in anaerobic soils or the persistence of aldicarb sulfide and aldicarb sulfone in aerobic soils.

2.1.3.5 Summary

Based on the above discussion and on the literature review by Cohen et al. (1984), the following conclusions can be tentatively made with respect to the most likely behavior of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in soil and water:

- o Based on theoretical considerations, aldicarb is unlikely to undergo significant rates of volatilization from natural waters under any conditions. No information is available on volatilization rates for aldicarb sulfoxide or aldicarb sulfone.
- o Based on theoretical considerations and limited data, volatilization may contribute significantly to the removal of aldicarb from the soil surface and from soil at shallow depths.
- o Based primarily on theoretical considerations, it is unlikely that transport by adsorption to suspended sediments or removal by adsorption to bottom sediments are important processes for either aldicarb or aldicarb sulfoxide.
- o Based upon theoretical considerations, leaching data and groundwater monitoring, it appears that aldicarb, aldicarb sulfoxide, and aldicarb sulfone are all susceptible to leaching from soils.
- o Hydrolysis does not appear to be an important removal process for aldicarb within the normal pH range of 6 to 9 (for natural waters) or for aldicarb sulfoxide and aldicarb sulfone at pHs less than 8. However, at pHs greater than 8, hydrolysis may become an important removal process for aldicarb sulfoxide and aldicarb sulfone.
- o Aldicarb appears to readily undergo oxidation to aldicarb sulfoxide and aldicarb sulfone in soils under aerobic conditions with a reported half-life of less than 1 week. Aldicarb sulfoxide and aldicarb sulfone are reported to readily undergo reduction to aldicarb sulfide in anaerobic soils. There was no information available on the persistence of aldicarb in anaerobic soils or the persistence of aldicarb sulfoxide and aldicarb sulfone in aerobic soils.

2.2 OCCURRENCE IN THE ENVIRONMENT

2.2.1 Water

This section presents available data from monitoring studies and surveys to determine the extent of occurrence of aldicarb and its transformation products, aldicarb sulfoxide and aldicarb sulfone, in public drinking water supplies and water other than drinking water.

2.2.1.1 Occurrence in Drinking Water

USEPA (1983a) summarized data on aldicarb in ground water samples collected near citrus groves in Florida. One sample from a possible drinking water source had a reported level of 3 to 5 ug/l aldicarb. The detection limit, number of samples, and number of positive samples were not reported.

2.2.1.2 Occurrence in Water Other Than Drinking Water

Three reports were identified that summarized data on aldicarb detected in ground water samples. Sample collection was conducted in several regions of the United States, mostly in high use areas.

Zaki et al. (1982, as cited in Cohen et al. 1984) reported on levels of aldicarb in ground water samples collected in 1982 from wells on Long Island, New York. Total aldicarb residues greater than the detection limit of 1 ug/l were found in ground water samples of 27 percent of 8,404 wells surveyed.

Cohen et al. (1984) reported data from unpublished EPA pesticide registration files, which showed aldicarb residues of 1 to 4 ug/l in ground water samples from wells in Oregon, Washington, Texas, and North Carolina. Samples of water from wells near a lily bulb farm in northern California showed aldicarb residues of up to 24 ug/l. The detection limit, number of samples, and number of positive samples were not reported for the sampling conducted in Oregon, Washington, Texas, North Carolina, and California. In an analysis of groundwater from nine wells in southern New Jersey, samples from three of the wells had aldicarb concentrations of 3, 4, and 50 ug/l; no detection limit was reported.

USEPA (1983a) summarized data on water samples collected since 1980 from wells in Wisconsin, Florida, Maine, Virginia, and North Carolina. Samples from approximately 4 percent of the wells studied had concentrations of aldicarb in excess of 10 ug/l. The detection limit, number of samples, and number of positive samples were not reported.

2.2.2 Occurrence in Ambient Air

No data were obtained on levels of aldicarb in ambient air.

2.2.3 Soil/Sediments

Only one study was identified that examined the occurrence of aldicarb in soils. Carey and Kutz (1983) presented data on soil samples collected at various depth intervals in areas treated with aldicarb in Florida and Mississippi. Of eight samples collected in Florida at depth intervals between 0 and 213 cm, all four samples collected at depths of 122 cm and greater contained detectable levels of aldicarb varying from 6,000 to 87,000 ug/kg, dry weight. None of the seven samples collected in Mississippi at depth intervals between 0 and 183 cm contained detectable levels of aldicarb. The minimum detection limit reported was 1,000 ug/kg aldicarb.

There were no studies identified that examined the occurrence of aldicarb in sediments.

2.2.4 Food

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the intake of various substances, including aldicarb, from foods consumed by adults, toddlers, and infants. The FDA provided mean daily intakes of aldicarb reflecting detections of aldicarb in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of aldicarb was 0.002 ug/day. For the 2-year old toddler, aldicarb intake was 0.006 ug/day. Aldicarb intakes for adult males and females are presented in Table 2-1. For the adult male, aldicarb intakes ranged between 0.008 and 0.018 ug/day. Daily aldicarb intakes for adult females ranged between 0.008 and 0.014 ug/day. Intakes were highest for the 60- to 65-year old age group of both sexes.

Table 2-1. Summary of FDA Total Diet Study Estimates For Adult Male and Female Aldicarb Intake

Sex/Age Group	Intake (ug/day)*
14-16 year old female	0.009
14-16 year old male	0.008
25-30 year old female	0.008
25-30 year old male	0.011
60-65 year old female	0.014
60-65 year old male	0.018

Source: FDA 1986.

2.3 EXPOSURE SUMMARY

While little or no data are available on the extent of aldicarb in drinking water, food, and air, a few limited surveys provide some useful information on occurrence. Monitoring surveys of groundwater (not specified as drinking water sources) in areas of high aldicarb use have reported levels of aldicarb and its metabolites in the range of 1 to 50 ug/l. These relatively high levels are the direct result of aldicarb's susceptibility to leaching from the soil column. Recent dietary studies report that the daily intake of aldicarb for 25- to 30-year old males ranged from 0.008 to 0.018 ug/day, with a mean daily intake of 0.011 ug/day. No data are available on aldicarb levels in ambient air. However, based on aldicarb's low vapor pressure, levels in air are expected to be negligible.

Because of the lack of monitoring data on aldicarb, and its degradation products in public water supplies, EPA is unable to make any estimates of exposure from drinking water. Based on monitoring data and physical and chemical properties of the compounds, dietary exposure is expected to be very low. Although no monitoring data are available, air levels of the compounds are also expected to be low. As a result of the expected low levels in food and air, if aldicarb occurs in drinking water, consumption of the water will be the major route of exposure.

3. CARBOFURAN

3.0 SUMMARY

Carbofuran is a widely used pesticide that has been shown to contaminate shallow ground water and surface water as a result of typical agricultural practices. The compound has been found in several states at levels as high as 65 ug/l.

3.1 GENERAL CHARACTERISTICS

3.1.1 Physical/Chemical Properties

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) is an insecticide/nematocide. Synonyms for carbofuran are Furadan, Yaltox, NIA-10242 ENT 27164, Bay 70143, Brifur, Crisfuran, Curaterr, D 1221, and FMC 10242 (Berg 1986).

Carbofuran is a white crystalline solid at 25°C (Windholz 1976). It has a molecular weight of 221.3, a molecular formula of $C_{12}H_{15}NO_3$, and a melting point of 150 to 153°C (Windholz 1976). The aqueous solubility of carbofuran at 25°C is 700 mg/l (3.2×10^{-3} mol/l) and its vapor pressure at 33°C is 2×10^{-5} torr (2.6×10^{-8} atm) (Verschueren 1983).

The ratio of the vapor pressure at 33°C to the aqueous solubility at 25°C gives an estimated Henry's constant for carbofuran at 25° to 33°C of 8.1×10^{-9} atm·m³/mol (2.9×10^{-8} torr l/mg). Reported K_{OC} values for carbofuran range from 29 to 63 (Cohen et al. 1984).

3.1.2 Use

Carbofuran is used as a broad spectrum carbamate insecticide, nematocide, and miticide (Berg 1986). Gianessi (1986) estimates that current use of carbofuran is about 8 million pounds.

Glaze estimated that in 1980 approximately 11 million pounds of carbofuran active ingredient were available for domestic usage and approximately 8 million pounds were exported (Glaze 1982).

Gianessi (1986) estimated that of the approximately 30 million pounds of carbofuran used nationwide from 1978 to 1982, 20 million pounds were applied to field corn and 4 million pounds were applied to sorghum. The remaining production was used on a large number of crops, including alfalfa, tobacco, peanuts, rice, sugarcane, potatoes, soybeans, sweet corn, cotton, grapes, and small grains.

3.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of carbofuran is divided into the following subsections: 3.1.3.1 Volatilization; 3.1.3.2 Sorption and Leaching Potential; 3.1.3.3 Abiotic Transformations; 3.1.3.4 Biodegradation; 3.1.3.5 Fate in Water Treatment Plants; and 3.1.3.6 Summary. The discussion will emphasize the environmental fate of carbofuran in soil and water.

3.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as carbofuran ($H = 8.1 \times 10^{-9} \text{ atm} \cdot \text{m}^3/\text{mol}$) with Henry's constants less than $3 \times 10^{-7} \text{ atm} \cdot \text{m}^3/\text{mol}$ are unlikely to undergo significant rates of volatilization from natural waters under any conditions normally found in the environment. Volatilization half-lives estimated by SAIC (see Appendix A) for carbofuran in shallow water under turbulent conditions support that conclusion. The estimated volatilization half-life for carbofuran in a turbulent lake 1 m deep with a mean current of 2 m/s and exposed to a mean wind velocity of 5 m/s are 27 years and 10 years, respectively. Volatilization rates of carbofuran from ground water to the soil column above are believed to be substantially less than volatilization rates from surface waters to the atmosphere. This is due primarily to the laminar, nonturbulent nature of ground water flow. Transport from ground water by volatilization may be further reduced by a build-up of chemicals in the pore air at the ground water/pore air interface, and an associated decrease in the concentration gradient across the interface.

The reported experimental volatilization half-life for carbofuran applied to a moist, loamy soil at 25°C and exposed to a wind speed of 1 km/s was 24 days (Swann et al. 1979, as cited in Cohen et al. 1984). This suggests that volatilization could be substantially involved in the removal of carbofuran from surface soils. The relatively low estimated volatilization half-life for carbofuran from soil surface compared to that for volatilization from water is due to the small value of the organic carbon normalized sediment or soil/water equilibrium partition coefficient (K_{OC}). Volatilization rates for carbofuran below the surface of the soil would probably be much slower than at the soil surface.

3.1.3.2 Sorption and Leaching Potential

Once released to surface water, carbofuran is expected to remain in solution and not to bind to suspended solids. The basis for this conclusion is provided in the following analysis.

Reported K_{OC} values for carbofuran range from 29 to 63 (Cohen et al. 1984). Substituting the median of the range of K_{OC} values (46) into equation A-11 of Appendix A gives estimated sediments or soil/water equilibrium partition coefficients ($K_{S/W}$) for carbofuran ranging from 0.46 to 3.7 for sediments or soils with organic fractions ranging from 0.01 to 0.08. The estimated $K_{S/W}$ values suggest that at equilibrium, the concentration of carbofuran in suspended and exposed bottom sediment may be comparable or even several times greater than that in water. However, as discussed in Appendix A, the $K_{S/W}$ value would probably have to be greater than 100 in most aquatic systems for the ratio of the chemical mass adsorbed to suspended and bottom sediments to the chemical mass dissolved in the water column to exceed 0.1. The reason is that in most aquatic systems most of the time, the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 10^3 .

Various experimental studies have shown that carbofuran is susceptible to leaching from a wide range of soils (USEPA 1984e). In addition, carbofuran has been detected at concentrations typically between 1 and 50 ug/l in a number of unconfined aquifer groundwater samples taken in Wisconsin and New York (Cohen et al. 1984).

3.1.3.3 Abiotic Transformations

Carbofuran has been shown to hydrolyze in water. The rate of hydrolysis is very dependent on pH. Reported hydrolytic half-lives for carbofuran in water are approximately 1 year at pH 6, 4 weeks at pH 7, and 1 day at pH 9 (Cohen et al. 1984). Based on these data, Cohen et al. (1984) suggest that the hydrolytic half-lives for carbofuran in groundwater would generally range from 2 to 50 weeks.

Seiber et al. (1978, as cited in USEPA 1984e) reported that the presence of sunlight increased the loss of carbofuran from rice paddy water and drainage ponds. No other information on the possible photolysis or oxidation by photochemically generated oxidants in water, soil, or air was found in the literature searched by USEPA (1984e).

3.1.3.4 Persistence in Soil

Based on a review of the literature, Cohen et al. (1984) indicate that half-lives of carbofuran in soils typically range from 1 to 37 weeks. It is classified as moderately persistent in soils (Rao and Davidson 1980) as opposed to persistent or nonpersistent. Degradation rates in soil appear to generally be greater in alkaline than in acidic soils and are generally greater in anaerobic or flooded soils than in aerobic soils (USEPA 1984e; Cohen et al. 1984).

3.1.3.5 Bioaccumulation

While no data have been identified on carbofuran's potential for bioaccumulation, the pesticide is not expected to bioaccumulate based on its physical and chemical properties. Carbofuran has been shown to hydrolyze in water and is not expected to persist in the environment for a sufficient period of time to bioaccumulate.

3.1.3.6 Fate in Water Treatment Plants

Based on limited data, USEPA (1985b) suggests that the following processes would be effective in removing carbofuran from drinking water: adsorption to activated carbon, reverse osmosis, and ozonation.

3.1.3.7 Summary

Based on the above discussion and the literature reviews by Cohen et al. (1984) and USEPA (1984e), the following conclusions can be made concerning the most likely behavior of carbofuran in soil and water:

- o Carbofuran is unlikely to undergo significant rates of volatilization from surface water or groundwater under any conditions normally encountered in the environment.
- o Volatilization appears to be a significant removal process for carbofuran on the soil surface. An experimental half-life of 24 days has been reported for carbofuran applied to a soil surface.
- o Based on theoretical considerations, the proportion of total carbofuran present in an aquatic system that is adsorbed to suspended and exposed bottom sediment is probably generally much less than the proportion dissolved in the water column.
- o Based on experimental results, carbofuran may be classified as at least moderately susceptible to leaching due to its low K_{oc} value.
- o Hydrolysis appears to be an important removal process for carbofuran in alkaline waters. Reported hydrolytic half-lives for carbofuran in water decrease with increasing pH from 1 year at pH 6 to 1 day at pH 9.
- o Reported and estimated half-lives for carbofuran in soils range from 1 to 37 weeks. Removal rates are generally greater in alkaline or anaerobic (flooded) soils than in acidic or aerobic soils.
- o Due to its moderate persistence and mobility in soils, carbofuran may contaminate some shallow unconfined aquifers or streams located near areas of carbofuran use.
- o The persistence of carbofuran in soil does not appear to be long enough to pose any long-term threat to water supplies in previously contaminated areas that are no longer being contaminated.

3.2 OCCURRENCE IN THE ENVIRONMENT

3.2.1 Water

This section presents available data from monitoring studies and surveys to determine the extent of occurrence of carbofuran in public drinking water supplies and water other than drinking water.

3.2.1.1 Occurrence in Drinking Water

No national studies were obtained addressing the occurrence of carbofuran in drinking water. However, three state studies were reviewed and are summarized below.

Ground Water Sources -- Regional Studies

In 1984, the Suffolk County Department of Health Services (Holden 1986) examined drinking water wells in Long Island, New York, for various pesticides. The survey sampled both public and private wells in close proximity to fields where carbofuran, aldicarb, and other pesticides were used. Of the 5,083 wells sampled, 1,535 contained detectable levels of carbofuran and 250 to 300 wells contained levels greater than 15 ug/l. The maximum level reported was 65 ug/l.

As part of a program of the Wisconsin Department of Natural Resources (Holden 1986), drinking water wells were also analyzed for carbofuran during 1983-1984. This statewide Wisconsin study examined wells suspected of contamination by both point and nonpoint sources. Of 78 samples analyzed, 2 were positive with a high concentration of 7 ug/l. No other information was reported.

Ground water wells were sampled near Richmond, Rhode Island, as part of a cooperative project between the U.S. Geological Survey and the Rhode Island Water Resources Board to identify potential drinking water sources for future water supply use (Offutt 1984). Eleven samples were collected during 1984 from five locations and analyzed for carbofuran. Seven were positive with a mean concentration of 3.7 ug/l (range = 2 to 7 ug/l). The detection limit was 1.0 ug/l.

3.2.1.2 Occurrence in Water Other Than Drinking Water

One national study of unidentified sources is reported for the occurrence of carbofuran. Four regional studies addressing levels of carbofuran in ground water and three surface water studies are also discussed here.

Ground Water Sources

Unpublished data summarized from EPA registration files and reported in Cohen et al. (1984) indicated that concentrations of carbofuran were present in samples of groundwater collected from private wells in areas with sandy soils and water table aquifers in Wisconsin and New York. Concentrations ranged from 1 to 50 ug/l carbofuran. The number of samples, number of positive samples, and detection limit were not reported.

Three studies were obtained examining groundwater wells in California. These studies were conducted by the California Department of Food and Agriculture in 1981, and again in 1982, and an evaluation in 1984 during the California State Board's Toxics Special Project (Ramlit Associates, Inc. 1983; Holden 1986; Cohen and Bowes 1984, respectively). Overall, approximately 30 counties were sampled for the occurrence of carbofuran. Over 200 samples were collected from as many sites, with only 2 proving positive. One concentration was 0.5 ug/l, the other was not reported. The detection limit for the sample concentration given above was also not reported.

Surface Water Sources

The Army Corps of Engineers sampled U.S. Geological Survey water stations along rivers of the Honey Creek watershed in northwest Ohio during 1981 (Datta no date). Carbofuran was sampled for at 12 locations and a maximum concentration of 45 ug/l was found. The number of samples, number of positives, and detection limit were not reported.

Dudley and Karr (1980, as cited in USEPA 1984d) presented data on levels of carbofuran in water, fish, and sediment samples collected from a stream draining the Black Creek agricultural watershed in Allen County, Indiana, during 1977-1978. Although the detection limit and the number of water samples collected and tested were not reported, none of the samples contained carbofuran in excess of the detection limit.

Woodham et al. (1975) presented monitoring data from a study to determine whether significant pesticide accumulation had occurred in two counties in North Carolina. Samples of pond water collected both inside and outside the

study area contained no carbofuran in excess of the detection limit of 0.05 ug/l.

Unidentified Sources

Water samples of unidentified sources were collected nationally from various studies and entered in the U.S. EPA's STORET data base (as reported in USEPA 1984e) during 1979 to 1982. Of the 21 stations sampled for carbofuran, 11 had undetectable levels. However, 58 samples were reported as positive. The total number of samples, detection limit(s), and range of positive values were not reported.

3.2.2 Occurrence in Ambient Air

No monitoring data that addressed levels of carbofuran in ambient air were found.

3.2.3 Soil/Sediments

Several studies have been identified that examine the occurrence of carbofuran in soil and sediments. Soil and sediment samples were collected from two counties in North Carolina where tobacco cropland had been treated. One soil sample contained 2,000 ug/kg of carbofuran; other soil samples contained less than 50 ug/kg of carbofuran. No residues of carbofuran were found in pond sediment samples in excess of the detection limit of 50 ug/kg (Woodham et al. 1975).

Samples of sediment collected from a stream draining an agricultural watershed in Indiana had no detectable levels of carbofuran (Dudley and Karr 1980, as cited in USEPA 1984d). The number of samples tested and the detection limit were not reported.

Kadoun and Mock (1978 as cited in USEPA 1984e) monitored sediment in tailwater pits collecting irrigation runoff in Haskell County, Kansas, in 1974. Carbofuran was detected in pit bottom sediments in four of 54 samples collected from 31 pits (four pits implicated) at mean levels between 30.6 and 50.0 ppb (max. 759 ppb).

3.2.4 Food

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the intake of various substances, including total carbofuran, from foods consumed by adults, toddlers, and infants. The FDA provided mean daily intakes of carbofuran reflecting detections of carbofuran in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of carbofuran was 0.0011 ug/day. For the 2-year old toddler, carbofuran intake was 0.005 ug/day. Total carbofuran intakes for adult males and females are presented in Table 3-1. For the adult male, carbofuran intakes ranged between 0.005 and 0.010 ug/day. Daily carbofuran intakes for adult females ranged between 0.006 and 0.013 ug/day. Intakes were highest for the 25- to 30-year old age group of both sexes.

TABLE 3-1. Summary of FDA Total Diet Study
Estimate for Adult Male and Female
Total Carbofuran Intake

Sex/Age Group	Intake (ug/day)*
14-16 year old female	0.006
14-16 year old male	0.005
25-30 year old female	0.013
25-30 year old male	0.010
60-65 year old female	0.006
60-65 year old male	0.008

Source: FDA 1986.

3.3 SUMMARY

Limited studies have been conducted that provide useful data on the extent of occurrence of carbofuran in drinking water, food, and air. Monitoring surveys of public water supplies have reported carbofuran levels as high as 65 ug/l in some high-use agricultural areas. Other regional studies typically reported maximum concentrations only as high as 7 ug/l. While some recent dietary studies report that the daily intake of carbofuran for 25- to

30-year old males and females is 0.010 and 0.013 ug/day, respectively, other studies have estimated that dietary levels may be as high as 460 ug/day. The actual range of intake of carbofuran in the diet is unknown. No data were found on carbofuran levels in ambient air. However, based on carbofuran's low vapor pressure and high water solubility, levels in air are expected to be very low.

According to the available monitoring data, the following limited conclusions can be made on the total exposure to carbofuran. Drinking water exposure in areas where carbofuran is used can result in intakes of greater than 100 ug/day. Typically, however, intakes of 10-15 ug/day may be expected. While dietary levels are not clearly defined, actual measurements suggest that for the majority of the population, intake levels are low. Inhalation intake is expected to be minimal.

4. CHLORDANE

4.0 SUMMARY

Chlordane is a nonpolar liquid that is currently used as a soil insecticide. In the environment, chlordane tends to bind to soil and to degrade slowly. Limited monitoring data are available for chlordane in drinking water. Because of its current use and its tendency to bind to soil, chlordane is expected to occur only at very low concentrations in drinking water, less than 0.01 ug/l. Because of the wide use of chlordane, it could potentially occur in all parts of the United States.

4.1 GENERAL CHARACTERISTICS

4.1.1 Physical/Chemical Properties

Chlordane (1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene) is a broad spectrum insecticide belonging to the group of chlorinated hydrocarbons known as cyclodiene insecticides (USEPA 1983b). Synonyms and identifiers for chlordane include the following (Berg 1986):

Belt	Kilex Lindane	Synklor
Chlor-Kil	Kypchlor	Termi-Ded
Chlortox	Niran	Topiclor 20
Corodane	Octachlor	Velsicol 1068
Gold Crest C-100	Octa-Klor	

Pure chlordane is a pale yellow liquid at 25°C composed of a 75:25 ratio of the cis and trans isomers (USEPA 1980a; Verschueren 1983). It is completely miscible in most organic solvents (Berg 1986). Chlordane has a molecular weight of 409.8 and a molecular structure of $C_{10}H_6Cl_8$ (Windholz 1976). The boiling points of the cis and trans isomers are 107 to 109°C and 103 to 105°C, respectively (Callahan et al. 1979). The pure chlordane mixture has an aqueous solubility and vapor pressure at 25°C of 5.6×10^{-2} mg/l (1.37×10^{-7} mol/l) and 1×10^{-5} torr (1.3×10^{-8} atm), respectively (Callahan et al. 1979).

Technical chlordane is a viscous amber liquid with a chlorine odor consisting of a mixture of 60 to 75 percent chlordane isomers and 25 to 40 percent

of 24 other organochlorine compounds (Berg 1986; Verschueren 1983). Technical chlordane has an aqueous solubility of approximately 9 ug/l (Verschueren 1983).

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant at 25°C for chlordane of 9.5×10^{-5} atm·m³/mol. The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant of 3.89×10^{-3} . Chlordane has an estimated K_{OC} value of 1.4×10^5 (Mabey et al. 1981).

4.1.2 Use

An EPA review of chlordane, begun in March 1971, concluded that this chemical is carcinogenic and that its use produces widespread contamination of the environment based on residues found in soil, air, water, food, wildlife, and man. On November 26, 1974, EPA published a notice of intent to cancel all registered uses of chlordane, except for subsurface ground insertion for termite control and dipping of roots and tops of nonfood plants. The EPA Administrator issued a notice of intent to suspend the registrations of certain products containing chlordane on July 25, 1975, and the final notice of suspension was issued on December 24, 1975. Cancellation proceedings continued through November 1977, at which time settlement negotiations began between EPA and the Velsicol Chemical Corporation.

The final cancellation order putting into effect the terms of settlement was issued on March 6, 1978 (USEPA 1983b; Kirk-Othmer 1979). In this agreement, the use of chlordane on food and other crops was to be phased out over a 5-year period. Underground termite control would be the only EPA-approved use of chlordane after 1980. In addition, all nontermite uses of chlordane during the phase-out period was restricted to treatment by certified applicators or professional commercial seed treatment companies (Chemical Regulation Reporter 1978).

Prior to its suspension and subsequent cancellation for most uses, chlordane was widely used as a pre-emergent insecticide for the control of corn rootworms, wireworms, and cutworms; as a soil treatment for the control of termites in structures; and as an insecticide for control of a variety of

pests on citrus, potatoes, strawberries, and tomatoes, and on lawns, gardens, turf, and ornamentals. Minor agricultural uses included applications to hay, tobacco, soybeans, vegetables, and peanuts (USEPA 1976).

Domestic production and use of chlordane has declined nearly 50 percent since 1974, when the EPA issued the notice of intent to cancel all agricultural uses of chlordane. However, the use of chlordane as a termiticide has continued, and chlordane is currently the most widely used insecticide for the control of subterranean termites in the United States according to the results of a risk/benefit analysis of chemicals used for subterranean termite control (USEPA 1983b). EPA estimated that 6.5 million pounds of chlordane were used for industrial/commercial purposes (primarily termite control) in 1972. The breakdown of use by region was: North Central, 1.6 million pounds; South Central, 1.3 million pounds; Southeast, 1.3 million pounds; Northeast, 1.0 million pounds; Southwest, 1 million pounds; and Northwest, 0.3 million pounds. In 1986 approximately 4 million pounds of chlordane were estimated to be used (Gianessi 1986). This figure is based on data obtained from various state, regional, and national pesticide usage surveys conducted by, USDA, USEPA, and the Department of Food and Agriculture of the State of California. USEPA (1983b) reported that the largest quantity was initially distributed in Region IV, which includes Alabama, Georgia, Florida, Mississippi, North Carolina, South Carolina, Tennessee, and Kentucky. Because chlordane is applied by subsurface ground injection, the potential for ground water contamination is high.

4.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of chlordane is divided into the following subsections: 4.1.3.1 Volatilization; 4.1.3.2 Sorption and Leaching Potential; 4.1.3.4 Abiotic Transformations; 4.1.3.4 Biodegradation and Persistence in Soil and Water; and 4.1.3.5 Summary. The discussion will emphasize the environmental fate of chlordane in soil and water.

4.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as chlordane ($H = 9.5 \times 10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}$) with Henry's constants exceeding $10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}$ are likely

to undergo significant rates of volatilization from surface waters under any conditions normally found in the environment. Volatilization half-lives estimated for chlordane in rivers or streams and turbulent lakes by SAIC using equations A-1 and A-3 through A-8 indicate that volatilization may be an important removal process for chlordane in shallow, turbulent waters, but may not be for some deep, stagnant waters depending on the relative rates of other removal processes such as adsorption to sediments with respect to volatilization. Estimated volatilization half-lives for chlordane in rivers or streams range from 12 hours in a shallow turbulent river or stream to 140 days in a deep low flow river or stream (see Appendix A). Estimated volatilization half-lives for chlordane in a turbulent lake range from 28 hours in a lake 1 m deep to 12 days in a lake 10 m deep. This analysis, however, does not reflect that chlordane will rapidly migrate to sediments where they will be adsorbed and thus will not be available for volatilization.

The volatilization rates of chlordane from groundwater to the soil column above are projected to be substantially less than volatilization rates from surface waters to the atmosphere. This is due primarily to the laminar, nonturbulent nature of groundwater flow. Volatilization rates from ground water may be further reduced by a build-up of chemical in the pore air at the ground water/pore air interface, and an associated decrease in the concentration gradient across the interface.

By substituting the estimated K_{OC} value for chlordane of 1.4×10^5 (Section 4.1) into equation A-9 along with the compound's vapor pressure (1×10^{-5} torr) and aqueous solubility (5.6×10^{-2} mg/l), SAIC estimates the volatilization half-life for chlordane on soil to be 12 days. Therefore, given the resistance of chlordane to chemical and biological degradation, volatilization could be an important removal process for chlordane on soil.

4.1.3.2 Sorption and Leaching Potential

Substituting the estimated K_{OC} value of 1.4×10^5 into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{s/w}$) for chlordane ranging from 1.4×10^3 to 1.1×10^4 for sediments or soils with organic carbon fractions ranging from 0.01 to 0.08. Therefore,

even though the ratio of the water mass to the mass of suspended and exposed bottom sediments exceeds 103 in most surface waters (USGS 1983), a substantial proportion of the total mass of chlordane may be adsorbed to suspended or exposed bottom sediments in many surface waters. Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are predicted generally to be important processes for chlordane in surface waters.

Substitution of the estimated K_{OC} value of 1.4×10^5 into equation A-13 gives an estimated soil TLC R_f value (Appendix A) of <0.10 . Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited in Hamaker (1975) for a soil with the same properties (Appendix A), chlordane would be expected to be immobile (Class 1) in, and extremely resistant to leaching from, surface soil.

4.1.3.3 Abiotic Transformations

Eichelberger and Lichtenberg (1971, as cited in Callahan et al. 1979) reported that greater than 97 percent of added chlordane was recovered from river water samples incubated at room temperature for 8 weeks. This suggests that neither hydrolysis nor biodegradation are significant removal processes for chlordane in natural waters.

Callahan et al. (1979) summarize reports that indicate that chlordane may be susceptible to photochemical sensitization that involves the decomposition of a compound via transfer of absorbed solar energy for naturally occurring organics. However, insufficient data are presented to estimate photodecomposition rates.

4.1.3.4 Biodegradation and Persistence in Soil and Water

Chlordane appears to be resistant to biodegradation not only in river water (Subsection 4.1.3.3), but in soil as well. Castro and Yoshida (1971) and Watanbe (1973), both as cited in Callahan et al. (1979), reported that chlordane is persistent in both flooded (anaerobic) and nonflooded (aerobic) soils. Rao and Davidson (1980) reported a degradative half-life for chlordane

in soil of approximately 3.3 years. Residues of chlordane may persist for 14 or more years after application at detectable levels, depending on the application rate and soil environment (USEPA 1980c). Therefore, chlordane appears to be extremely persistent in soils.

4.1.3.5 Summary

Based on the above discussion and the literature review by Callahan et al. (1979), the following tentative conclusions can be made concerning the most likely behavior of chlordane in soil and water:

- o Based on theoretical considerations, limited data, and the apparent resistance of chlordane to hydrolysis and biodegradation, volatilization along with adsorption to suspended and bottom sediments are predicted to be the major removal mechanisms for chlordane in surface waters.
- o Based on theoretical considerations, chlordane is predicted to be highly resistant to leaching from surface soils.
- o Based upon limited data, chlordane appears to be resistant to both hydrolysis and biodegradation in river water. It may be somewhat susceptible to photodecomposition via photochemical sensitization, but no rates are available.
- o Based on several soil studies and on the observed persistence of chlordane residues in soils at detectable levels for many years after application, chlordane can be classified as extremely persistent in soils.

4.2 OCCURRENCE IN THE ENVIRONMENT

4.2.1 Water

The following section presents the data available from monitoring studies and surveys to determine the extent of occurrence of chlordane in public drinking water supplies and water other than drinking water.

4.2.1.1 Occurrence in Drinking Water

Ten regional studies of chlordane in drinking water are addressed in this section. Where possible, groundwater sources and surface water sources have been discussed separately.

Ground Water Sources

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. None of the 100 ground water supplies sampled, representative of the 5 aquifers in Florida, contained measurable levels of chlordane (no detection limit was reported).

Less than 8 percent of samples from 96 locations utilizing the Floridan aquifer were found positive for chlordane, in a 1984 study by the Florida Department of Environmental Resources and the U.S. Geological Survey (Holden 1986). These supplies serve over three million people. No other information from the study was reported.

No positive samples were found for chlordane in the following two studies; one involved the 1984-1985 sampling of 42 sites from 12 towns in Connecticut and the other involved the analysis of 67 samples from Long Island, New York, in 1984 (Waggoner 1985; Holden 1986). The Connecticut drinking water wells serve a population of over 570,000, and the detection limit for that study was 3.3 ug/l. No other information about either study was reported.

Two positive samples (one for alpha chlordane and one for gamma-chlordane) out of 107 samples analyzed were found for groundwater wells in Idaho (Idaho Department of Health and Welfare 1984). Monitoring for pesticides in drinking water wells is not routinely done; the sampling performed was in response to a particular contamination incident, not for any comprehensive monitoring program. A relatively low mean of 0.0002 ug/l was reported for these two samples, with one sample having a chlordane concentration of 0.038 ug/l (no detection limit was reported). It appears that "negative" samples, possibly assigned a detection limit value, were included in the calculation of the mean.

Benvenue et al. (1972b, as cited in Cirelli 1978) conducted a study to determine the extent of organochlorine pesticide contamination of drinking water in Hawaii. A total of 45 finished drinking water samples were collected from February 1971 to May 1971. Concentrations of chlordane were detected in four of the samples, with a range of positive values between 0.0005 and 0.005 ug/l, and an average concentration of 0.001 ug/l (no detection limit was reported).

Surface Water Sources

Irwin and Healy (1978), summarizing data collected during a water quality reconnaissance of public water supplies in Florida, reported that none of the 16 surface water supplies sampled contained chlordane in excess of the detection limit. No detection limit was reported.

In the New Orleans Water Supply Study conducted by USEPA Region VI (USEPA 1975a), samples of drinking water were analyzed for levels of halogenated organics. Although the number of positive samples was not reported, the concentrations of chlordane in three samples analyzed ranged from "non-detected" to less than 0.1 ug/l. No detection limit for the analyses was reported.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic

parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including chlordane, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

Unspecified Sources

Two regional studies identified levels of pollutants in drinking water from unspecified sources. A Region V Survey (USEPA 1975b), conducted during the first three months of 1975, assessed levels of organic chemicals in samples of raw and finished drinking water collected from 83 utilities in Indiana, Illinois, Michigan, Minnesota, Ohio, and Wisconsin. Samples were analyzed for various pollutants including gamma-chlordane. One sample of finished drinking water contained gamma-chlordane at a level of 0.004 ug/l. No limits of detection for pesticides were reported.

In a study to identify the sources of pollutants entering a sewage treatment plant, Levins et al. (1979a) collected samples from two drinking water sources. Although no detection limit was reported, the analyses detected no chlordane in any of the samples.

Schafer et al. (1969, as cited in USEPA 1980a) reported concentrations of chlordane up to 8 ug/l for finished drinking waters, although no location(s) were given. No other information on this study was reported.

4.2.1.2 Occurrence in Water Other Than Drinking Water

Two national studies and seven regional studies analyzed concentrations of chlordane in water other than drinking water.

Ground Water Sources -- Regional Study

Tucker and Burke (1978) reported the results of a statewide ground water monitoring project conducted in New Jersey. For this study, samples of water were collected from 163 wells in nine counties. The analysis showed that samples of water from five wells contained levels of chlordane in excess of the minimum reportable concentrations of 0.01 ug/l. The range of positive values was 0.01 to 0.02 ug/l chlordane.

One California study of ground water wells found four samples, from as many counties, positive for chlordane with a maximum value of 22 ug/l. No other data were presented for this study. One of three well samples collected in the Barstow, California, area was found to have a chlordane concentration of 0.4 ug/l by the Victorville Regional Water Quality Board in 1980 (Ramlit Associates, Inc. 1983).

Surface Water Sources -- National Study

The National Pesticide Monitoring Network (Gilliom et al. 1985) examined surface water samples from rivers nationwide during 1975-1980, and found no positive samples of chlordane out of 2,943 samples analyzed from 177 locations. The detection limit was 0.15 ug/l.

The National Surface Water Monitoring Program (Carey and Kutz 1983) presented data on levels of chlordane in surface water samples collected throughout the United States between 1976 and 1980. Although no detection limit for chlordane was reported, 1.1 percent of the samples analyzed had detectable concentrations of chlordane, with a maximum reported value of 0.23 ug/l. The number of samples taken was not reported. It is not known whether the samples were filtered or unfiltered.

Surface Water Sources -- Regional Studies

Truhlar and Reed (1976) reported the results of analysis of water samples taken from four streams in Pennsylvania. The streams drained four types of land use areas: forests, general farms, orchards, and residential areas.

None of the 19 samples collected and analyzed from April 1970 to February 1971 contained chlordane in excess of the detection limit. The detection limit was not reported.

Benvenue et al. (1972b, as cited in Cirelli 1978) conducted extensive sampling of two canals on Oahu, Hawaii, to determine the extent of organo-chlorine pesticide contamination. A total of nine samples were collected from two canals and analyzed for residues of chlordane. The analyses showed an average concentration of chlordane of 0.007 ug/l and a range of positive values of 0.003 to 0.018 ug/l. The number of positive samples and the detection limit were not reported.

Barks (1978) presented the results of a USGS water quality study conducted from April 1973 to July 1974 in the Ozark National Scenic Riverways, Missouri. During the study, 20 surface water samples were collected from 3 sites on the Current River and 1 site on Jacks Fork and analyzed for pesticide content. None of the unfiltered samples contained concentrations of chlordane in excess of the detection limit (no detection limit was reported).

Englande et al. (1978) presented the results of extensive chemical analyses of six Advanced Wastewater Treatment (AWT) plant effluents. The plants were located in California, the District of Columbia, and Texas. A mean concentration of less than 0.039 ug/l chlordane was identified in one plant effluent; the other systems had no detectable levels of chlordane. The number of positive samples and the detection limit were not reported.

4.2.2 Occurrence in Ambient Air

Results of the Suburban Air Sampling Program of the National Pesticide Monitoring Program for 1975 were reported in Kutz et al. (1976) and SRI (1983). Samples were collected at three suburban locations during April (two samples), May (four samples), and June (four samples). Concentrations of chlordane were detected in eight samples from a city in Florida, with a mean of 0.015 ug/m³ and a range of "not detected" to 0.026 ug/m³. A mean of 0.035 ug/m³ and a range of trace to 0.059 ug/m³ were reported for samples collected from a city in Mississippi. All ten samples were positive. No chlordane was

of the detection limit (the detection limit was not reported). Only one sample of the 21 sediment samples collected and analyzed contained chlordane. The sample was collected from a stream draining a residential area and contained 250 ug/kg chlordane. No detection limit for the analyses was reported.

Several reports addressed levels of chlordane in stream bed sediments. Britton et al. (1983) reported on levels of pesticides in water-sediment mixtures (unfiltered samples) and in bottom material samples collected by the National Stream Quality Accounting Network (NASQAN) in 1976. Throughout the United States, 151 permanent stations plus stations added as part of local programs were sampled for pesticides, including chlordane. Water-sediment samples were collected quarterly; bottom material samples were collected semiannually. Chlordane was detected in water-sediment samples collected at three of six stations in California; the maximum chlordane level found at these stations was 1.7 ug/kg. Concentrations of chlordane in excess of the detection limit were reported in 24 of 153 bottom material samples collected from 13 different regions (the detection limit was not reported). The maximum level found at these stations was 333 ug/kg.

Carey and Kutz (1983) summarized data on pesticide residues in sediment samples collected by the National Surface Water Monitoring Program (NWMP) from 1976 to 1980. Chlordane was detected in 15.3 percent of the sediment samples analyzed; the maximum reported value was 2,964 ug/kg. No information was available regarding the detection limits of analysis.

4.2.5 Food

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the intake of various contaminants, including chlordane, from foods consumed by adults, toddlers, and infants. The FDA provided mean daily intakes of chlordane reflecting detections of chlordane in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month infant, the daily intake of chlordane was 0.016 ug/day. For the 2-year old toddler, chlordane intake was 0.019 ug/day. Intakes of chlordane by adult males and females are presented in Table 4-1. For the adult male, chlordane intakes ranged between 0.024 and 0.081 ug/day.

Daily chlordane intakes for adult females ranged between 0.025 and 0.070 ug/day. Intakes were highest for the 60- to 65-year old age group of both sexes.

Table 4-1. Summary of FDA Total Diet Study Estimates for Chlordane Intakes from Adult Males and Females.

Sex/Age Group	Intake (ug/day)
14-16 year old female	0.025
14-16 year old male	0.024
25-30 year old female	0.048
25-30 year old male	0.044
60-65 year old female	0.070
60-65 year old male	0.081

Source: FDA 1986.

4.3 EXPOSURE SUMMARY

While few current data are available on the extent of occurrence of chlordane in drinking water, air, and food, several limited surveys provide some useful information. Chlordane is very persistent in the soil column and consequently, can pose a long-term but low-intensity threat to groundwater supplies. As a result of this low-intensity threat, the maximum reported level of chlordane in drinking water is only 0.005 ug/l. Data on the occurrence of chlordane in ambient air are also limited. Even during the early and mid-1970's when chlordane was widely used as an agricultural insecticide, outdoor air levels were low, with a reported maximum value of 0.059 ug/m³. Current ambient air levels are likely to be less because today's uses have less potential for release into the air. However, potential does exist for indoor air exposure because chlordane is often injected directly into a house's foundation to fight termites. Unfortunately, current data reflecting this practice are not available.

Recently dietary studies report the mean daily intake of chlordane for 25-30 year old males to be 0.044 ug/day. Earlier dietary studies reflected the presence of pesticide residues on the samples. However, with the ban of chlordane in 1978, this source of contamination was eliminated. Consequently, dietary levels of chlordane are less today than in 1978.

TABLE 4-2

Route	Reported Exposure Levels	Estimated Adult Intakes
Drinking Water	<0.1 ug/l	<0.2 ug/day
Diet	--	0.044 ug/day
Air	*	--

*Ambient air levels of the compounds are believed to be very low. Indoor air levels, although unknown, are expected to be higher than outdoor.

The information that is currently available on the occurrence of chlordane in the environment and the potential for exposure are insufficient to determine the national distribution of intake of chlordane by any of the three routes. Because data reported for drinking water diet and air exposure levels were derived from studies conducted during the early 1970s to the mid 1980's (prior to the restriction of most uses of chlordane), current levels from all three sources are expected to be minimal. However, additional data are needed to evaluate current exposure levels and to provide a comparable basis for estimating the total combined intake from each media.

5. DBCP

5.0 SUMMARY

DBCP is a chemical that has been widely used as a soil fumigant. As a result of this use, DBCP contamination has been detected in a number of groundwater wells at levels of several ug/l. Due to the cancellation of most of DBCP's uses in the last 10 years, production of this chemical has greatly declined. Because of the current low level of use, DBCP is not expected to be a common contaminant of drinking water supplies.

5.1 GENERAL CHARACTERISTICS

5.1.1 Physical/Chemical Properties

DBCP (1,2-dibromo-3-chloropropane) is a soil fumigant. Synonyms for DBCP included BBC 12, Fumazone, Nemagon, Nemanax, Nemaset, Nematocide, and Oxy DBCP (Berg 1986).

DBCP is an amber to dark brown liquid at 25°C (Verschuieren 1983). It has a molecular weight of 236.36, a melting point of 6°C, and a boiling point of 196°C (Windholz 1976). The aqueous solubility and vapor pressure of DBCP at 21°C are 1,000 mg/l (4.2×10^{-3} mol/l) and 0.8 torr (1.1×10^{-3} atm), respectively.

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant for DBCP at 21°C of 2.6×10^{-4} atm·m³/mol (8.0×10^{-4} torr l/mg). The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant of 1.08×10^{-2} . Reported K_{OC} values for DBCP include 55, 119, 129, and 149 (Cohen et al. 1984).

5.1.2 Use

DBCP was used as a soil fumigant for nematode control (Berg 1986). Although domestic production figures could not be obtained, an estimated

32,658,000 pounds of DBCP active ingredient were used in 1977. In that year, the three major domestic producers of DBCP voluntarily curtailed production (USDA 1978). This action on the part of the three domestic producers came as a result of the EPA's decision on November 3, 1977 to greatly curtail the uses of DBCP on 19 crops (42 FR 57543). On October 29, 1979, the EPA Administrator issued the Agency's final decision to suspend unconditionally the registrations of DBCP for all uses except on pineapple fields in Hawaii (44 FR 65161; USEPA 1984h).

As noted above, DBCP registrations for all uses except on pineapple fields in Hawaii were suspended by EPA on October 29, 1979. Of the approximately 43,000 acres devoted to the production of pineapples in Hawaii, 5,000 acres were treated in 1977 with approximately 665,200 kg of DBCP at a rate of 133 kg of active ingredient per acre (USDA 1978). Cancellation proceedings are currently under consideration for the use of DBCP on pineapple fields in Hawaii, on the basis of recently acquired information indicating that the use of DBCP as a soil fumigant has led to the contamination of ground water aquifers used as sources of drinking water (USEPA 1984h).

5.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of DBCP is divided into the following subsections: 5.1.3.1 Volatilization; 5.1.3.2 Sorption and Leaching Potential; 5.1.3.4 Abiotic Transformations; 5.1.3.4 Biodegradation and Persistence in Soil and Water; and 5.1.3.5 Summary. The discussion will emphasize the environmental fate of DBCP in soil and water.

5.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as DBCP ($H = 2.6 \times 10^{-4}$ atm·m³/mol) with Henry's constants greater than 10^{-4} atm·m³/mol are likely to undergo significant rates of volatilization from surface waters under any conditions normally found in the environment. Volatilization half-lives estimated for DBCP in rivers or streams and turbulent lakes by SAIC using equations A-1 and A-3 through A-8 indicate that volatilization is an important process for DBCP in shallow turbulent waters, but may not be for some deep

stagnant waters, depending on the relative rates of other removal processes with respect to volatilization. Estimated volatilization half-lives for DBCP in rivers or streams range from 3.7 hours in a shallow turbulent river or stream to 86 days in a deep low flow river or stream (see Appendix A). Estimated volatilization half-lives for DBCP in turbulent lakes range from 16 hours in a lake 1 m deep to 6.6 days in a lake 10 m deep.

The volatilization rates of DBCP from groundwater to the soil column above are projected to be substantially less than volatilization rates from surface waters to the atmosphere. This is due primarily to the laminar, nonturbulent nature of groundwater flow. Volatilization rate from ground water may be further reduced by a build-up of chemical in the pore air at the ground water/pore air interface, and an associated decrease in the concentration gradient across the interface.

By substituting a mean K_{OC} value for DBCP of 113 (Section 5.1.1) into equation A-9 along with the compound's vapor pressure (0.80 torr) and aqueous solubility (1,000 mg/l), SAIC estimates the volatilization half-life for DBCP on the soil surface to be 3.2 minutes. Therefore, volatilization from the soil surface is predicted to be extremely rapid. Even though volatilization rates of DBCP in soil beneath the surface would be much slower, the extremely rapid estimated volatilization rates from the soil surface suggest that volatilization could be an important removal process for DBCP beneath the soil surface as well.

5.1.3.2 Sorption and Leaching Potential

Substituting the mean K_{OC} value of 113 into equation A-11 gives estimated sediment or soil/water partition coefficients ($K_{S/W}$) for DBCP ranging from 1.1 to 9.0 for sediments or soils with organic carbon fractions ranging from 0.01 to 0.08, respectively. Since the estimated $K_{S/W}$ values for DBCP are less than 10, it is unlikely that the ratio of the total mass of DBCP adsorbed to suspended and exposed sediments to the total mass of DBCP dissolved in the water column will exceed 0.01 in most surface waters. The reason is that in most surface waters most of the time, the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 1,000 (USGS 1983). Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are probably not important processes for DBCP in surface waters.

Substitution of the mean K_{oc} value of 113 into equation A-13 gives an estimated soil TLC R_f value (Appendix A) of 0.44 for DBCP adsorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), DBCP would be expected to have an intermediate mobility (Class 3) in, and to be intermediate between being moderately susceptible and moderately resistant to leaching from, surface soil. However, DBCP has been detected in groundwater samples from several states including Hawaii, California, Arizona, South Carolina, Maryland, and Alabama (Cohen et al. 1984; Carey and Kutz 1983). In Hawaii, an aquifer that lay several hundred feet beneath the surface was contaminated. In one California study, DBCP was reported to have leached 15 m through the unsaturated zone (Nelson et al. 1981, as cited in Cohen et al. 1984).

5.1.3.3 Abiotic Transformations

Hydrolysis half-lives for DBCP at pH 7 are reported to be 141 years at 15°C and 38 years at 25°C (Burlinson et al. 1982). Estimated hydrolysis half-lives for DBCP at pH 9 range from 5 years at 15°C to 0.6 years at 25°C (Deeley 1986). Therefore, hydrolysis does not appear to be a significant removal process for DBCP in natural waters. No information on photolysis or oxidation is available. However, since DBCP does not have any chromophores that absorb light strongly above the approximate solar radiation cutoff at the earth's surface of 290 nm nor a functional group susceptible to oxidation, it is unlikely that DBCP undergoes significant rates of direct photolysis or oxidation in the environment.

5.1.3.4 Biodegradation and Persistence in Soil and Water

Under optimal laboratory conditions in a bioactive agricultural soil, DBCP was reported to have a degradation half-life of approximately 10 weeks (Castro and Belser 1968, as cited in Cohen et al. 1984). Based on that, DBCP would be classified as moderately persistent (half-life between 20 and 100 days) in soil under optimal conditions (Rao and Davidson 1980). No other information on biodegradation was available in the literature reviewed by Cohen et al. (1984).

5.1.3.5 Summary

Based on the above discussion and on the literature review by Cohen et al. (1984), the following tentative conclusions can be made concerning the most likely behavior of DBCP in soil and water:

- ° Based upon theoretical considerations and reportedly low hydrolysis rates, volatilization is expected to be the primary mechanism of DBCP removal in surface waters and on the soil.
- ° Based upon theoretical considerations, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are not expected to be important processes for DBCP in aquatic systems.
- ° Based upon theoretical considerations, leaching data, and groundwater monitoring, DBCP appears to be at least moderately susceptible to leaching.
- ° Reported hydrolysis half-lives for DBCP at pH 7 exceed 10 years. Therefore, hydrolysis does not appear to be an important removal process for DBCP in water. No information is available on photolysis or oxidation. However, based on its chemical structure, DBCP is not expected to undergo significant rates of photolysis or oxidation in the environment.
- ° Under optimal conditions in a bioactive agricultural soil, DBCP is reported to have a degradation half-life of 10 weeks, which corresponds to a classification of relatively persistent in soils.
- ° Due to its estimated rapid volatilization from most surface waters, DBCP is not expected to significantly contaminate surface water supplies.

5.2 OCCURRENCE IN THE ENVIRONMENT

5.2.1 Water

This section presents available data from monitoring studies and surveys to determine the extent of occurrence of DBCP in public drinking water supplies and water other than drinking water.

5.2.1.1 Occurrence in Drinking Water

Only one regional study was found that addressed levels of DBCP in samples of drinking water obtained from groundwater and surface water sources.

Groundwater Sources

Carey and Kutz (1983) presented data collected in 1979 on levels of DBCP in ground water samples collected in California, Arizona, Texas, South Carolina, and Alabama. Eight positive ground water samples collected from California and South Carolina showed DBCP concentrations ranging from 0.01 ug/l to 10.8 ug/l, and an average concentration of 2.8 ug/l. Seven of the positive samples were from private wells; one sample containing 0.01 ug/l was from a municipal well. The number of ground water samples tested was not reported.

Surface Water Sources

Carey and Kutz (1983) also reported on levels of DBCP in samples of surface water collected in California, Arizona, Texas, South Carolina, and Alabama in 1979. Two positive samples collected from municipal water supplies in California showed DBCP concentrations of 0.09 ug/l and 0.1 ug/l. The number of surface water samples tested was not reported.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals,

pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including DBCP, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

5.2.1.2 Occurrence in Water Other Than Drinking Water

Several regional studies (Peoples et al. 1980; Nelson et al. 1981; Pinto 1980; Cohen 1981; Carter and Riley 1981; and Mink 1981, all as cited in Cohen et al. 1984) and the EPA pesticide registration files, as reported in Cohen et al. (1984), provided monitoring data on levels of DBCP in ground water. Positive concentrations of DBCP ranging from 0.02 ug/l to 20 ug/l were detected in samples of ground water in Hawaii, California, Arizona, South Carolina, and Maryland. Areas with the highest concentrations were the San Joaquin Valley in California and the region southwest of Phoenix, Arizona. The number of samples analyzed, the number of positive samples detected, and the detection limit were not reported.

Holden (1968) reported that, in a massive survey of more than 8,000 public and private wells in the San Joaquin Valley of California, detectable levels of DBCP were found in approximately 25% of the wells tested. The highest level of DBCP found in the survey was 1,240 ug/l.

Samples of groundwater collected from seven previously unsampled sites in Hawaii showed detectable levels of DBCP in the range of 0.05 ug/l to 0.5 ug/l (USEPA 1984h). Some of the sites have been used as drinking water supplies. The number of samples tested, the number of positive samples, and the detection limit were not reported.

5.2.2 Occurrence in Ambient Air

Pellizzari and Bunch (1979) analyzed seven air samples in El Dorado, Arkansas, for DBCP. Six of the seven samples were DBCP positive, with mean and median concentrations of 0.0064 and 0.0018 ug/m³, respectively, and a maximum detected concentration of 0.014 ug/m³.

5.2.3 Soil/Sediments

Minimal information was available on studies that had been conducted to determine the occurrence of DBCP in soil and sediments. Two such studies were identified, both involving soil sample collection. No sediment studies were identified.

Analysis of California soil cores collected by Nelson et al. (1981, as cited in Cohen et al. 1984) showed ug/kg amounts of DBCP that had leached 15 m through the unsaturated zone. Analysis of additional California soil cores collected by Zalkin et al. (1983 as cited in Cohen et al. 1984) detected no DBCP in soil cores collected as deep as 10 m, 4 years after the last DBCP application, indicating rapid downward movement of DBCP in the soil. In both studies, the number of samples tested, the number of positive samples detected, and the detection limit were not reported.

5.2.4 Food

Several studies were identified that examined the occurrence of DBCP in food in the United States. These studies are summarized here.

Monitoring data provided by Del Monte Corporation and the FDA showed no detectable residues of DBCP in a variety of samples analyzed (USEPA 1984h). However, these residue data are "limited in scope." The number of samples analyzed and the detection limit were not reported.

USDA (1978) presented data from several sources on DBCP residues in a variety of raw agricultural commodities. Newsome et al. (1977, as cited in USDA 1978) detected DBCP residues ranging from 20 to 1,500 ug/kg in carrots

grown in fumigated soil. The detection limit, the number of samples analyzed, and the number of positive samples were not reported.

The Shell Chemical Company provided data on levels of DBCP in raw agricultural commodities. Residues of DBCP in the range of 10 to 1,120 ug/kg were detected in broccoli, cabbage, cauliflower, and cucumbers. Additional monitoring data provided by Dow Chemical Company identified residues of DBCP in peanut kernels in the range of 10 to 140 ug/kg. The number of samples analyzed, the number of positive samples detected, and the detection limit were not provided (USDA 1978).

In its compliance program report for FY 79 on pesticides and metals, the FDA (1982c) presented data on levels of DBCP in samples of domestic and imported fish. A total of seven of 1,515 fish samples analyzed contained levels of DBCP in excess of the detection limit. The seven positive values were from domestic fish samples; the maximum value reported was "trace" (detection limit not given).

No detectable levels of DBCP were found in peaches or pineapples grown in DBCP-treated areas during the FDA's FY79 surveys (FDA 1981b). The detection limit for these studies was not reported.

The data obtained on levels of DBCP in food were insufficient for use in estimating the typical dietary intake of DBCP.

5.3 EXPOSURE SUMMARY

Current data are unavailable on the extent of occurrence of DBCP in drinking water, food, and air. According to the monitoring data collected during the late 1970's when DBCP use was still widespread, contamination of surface water supplies was minimal because of the compounds high volatility. However, due to its moderate susceptibility to leaching from the soil column, DBCP levels in some groundwater supplies ranged from 0.01 to as high as 10.8 ug/l. Because these surveys, while limited, were performed in areas of high DBCP usage and because very little DBCP has been released to the environment since 1977, current levels are not expected to exceed those of the earlier surveys. The available food and air data are no longer valid for estimating exposure to DBCP because most of the data were collected before DBCP was restricted. However, current intake levels are expected to be minimal.

6. 2,4-D

6.0 SUMMARY

2,4-D (2,4-dichlorophenoxy) acetic acid) is a widely used systemic herbicide. Large amounts of 2,4-D and its esters are used in household and agricultural herbicide products. Because of 2,4-D's tendency to bind to soils and to degrade relatively rapidly, levels in drinking water are low. Surveys of 2,4-D in drinking water have found that when the compound occurs at detectable levels the concentration does not exceed 1 to 2 ug/l.

6.1 GENERAL CHARACTERISTICS

6.1.1 Physical/Chemical Properties

2,4-D (2,4-dichlorophenoxy) acetic acid) is a systemic herbicide. The term 2,4-D includes the parent acid as well as the 35 derivatives (esters and salts) (USEPA 1982d). Only a small amount of the parent acid is used commercially. Synonyms and identifiers for 2,4-D, which are numerous, include Agrotect, Aqua Kleen, Dinoxol, Estone, Herbidal, Salvo, Weedone, Weed-B-Gon, Tributon, Transamine, and Miracle (Berg 1986).

2,4-D is a white powder at 25°C (Verschuieren 1983). It has a molecular weight of 221.04, a molecular formula of $C_8H_6Cl_2O_3$, and a melting point of 138°C (Windholz 1976). The aqueous solubility of 2,4-D is 890 mg/l at 25°C (Verschuieren 1983) and its vapor pressure at 25°C is 6.0×10^{-7} torr (Laskowski et al. 1982). The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant at 25°C for 2,4-D of 2×10^{-10} atm·m³/mol. Reported K_{OC} values for 2,4-D include 20 (Rao and Davidson 1980) and 32 (Hamaker 1975). The pK_a value for 2,4-D is 2.80.

The aqueous solubility and vapor pressure at 25°C of the n-butyl ester of 2,4-D are 1 mg/l and 3.9×10^{-4} torr, respectively (Zepp et al. 1975). The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant for the n-butyl ester of 2,4-D of 1.6×10^{-4} atm·m³/mol. No information on the physical/chemical properties of other esters of 2,4-D could be found in the literature.

6.1.2 Use

An estimated 60 to 75 million pounds of 2,4-D active ingredient were produced annually in the United States. Imports and exports of 2,4-D are estimated at 3 to 5 million and 10 to 15 million pounds, respectively. Actual domestic usage of 2,4-D in 1986 was 60 million pounds (Kuch 1986). Gianessi (1986) reported approximately 40 million pounds used in a 33-state area.

Registered uses of 2,4-D include post-emergent weed control in grasses, wheat, barley, oats, sorghum, corn, sugarcane, and rice. Certain formulations are registered for pine release, water hyacinth control, and prevention of seed formation, and other formulations are registered for broadleaf control in cereal grains (Berg 1986).

An estimated 15 to 20 million pounds of 2,4-D active ingredient (approximately 31 to 32% of the total amount of 2,4-D estimated to have been used in 1980) was applied to wheat (Kuch 1980). The USDA reported that 5.1 million pounds of 2,4-D were used on field corn nationwide in 1982 (USDA 1983).

Rangeland and pastureland throughout the United States were treated with between 10 and 12 million pounds of 2,4-D in 1980 (Kuch 1980); 46,500 pounds of 2,4-D were used in 1982 on California rangelands (California 1982).

In 1980, between 6 and 7 million pounds of 2,4-D were applied to sites such as airfields, driveways, equipment yards, fencerows, implement storage yards, incineration areas, industrial yards, loading areas and ramps, mills, oil tank farms, parking areas, pole yards, sidewalks, warehouse plant sites, vacant lots, and around buildings and water meters.

EPA reported the use of 3 to 3.5 million pounds of 2,4-D nationwide on lawns and turf in 1980 (Kuch 1980). EPA has registered the use of 2,4-D on bahaigrass, bentgrass, bermudagrass, bluegrass, carpetgrass, centipedegrass, dichondra, fescue, red top, St. Augustine grass, zoysia grass, and golf courses.

An estimated 4 to 6 percent of the total domestic usage of 2,4-D in 1980 (2-3 million pounds) was applied to aquatic areas throughout the United States. EPA has registered 2,4-D as an herbicide to control weeds in and around lakes and ponds (impounded water); in marshes, estuaries, and shore lines; along ditch banks, drainage ditch banks, and irrigation ditch banks (adjacent to water); and in nonpotable water, drainage ditches, drainage and irrigation systems, streams, and waterways (Kuch 1980).

According to EPA, the following uses of 2,4-D in 1980 represented only 4 percent of the total domestic usage for that year: sugar cane, rice, barley, soybeans, almonds, sweet corn, sunflowers, apples, pecans, pears, peanuts, cherries, citrus, peaches, plums and prunes, walnuts, and forestry (Kuch 1980).

6.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of 2,4-D is divided into the following subsections: 6.1.3.1 Volatilization; 6.1.3.2 Sorption and Leaching Potential; 6.1.3.3 Abiotic Transformations; 6.1.3.4 Biodegradation and Persistence in Soil and Water; and 6.1.3.5 Summary.

2,4-D is applied as an acid and as various esters and amine salts of the acid compound. In the environment, the n-butyl ester appears to undergo rapid hydrolysis to 2,4-D (Zepp et al. 1975). This discussion will emphasize the environmental fate of 2,4-D in soil and water.

6.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as 2,4-D ($H = 2.0 \times 10^{-10} \text{ atm}\cdot\text{m}^3/\text{mol}$) with a Henry's constant less than $3 \times 10^{-10} \text{ atm}\cdot\text{m}^3/\text{mol}$ are less volatile than water. Therefore, the concentration of 2,4-D in water is not expected to decrease at all due to volatilization.

Substitution of the mean reported Koc value of 26 for 2,4-D into equation A-9 along with the compound's aqueous solubility (890 mg at 25°C) and vapor pressure (6.0×10^{-7} torr at 25°C) gives an estimated volatilization half-life of 1.7 years for 2,4-D on the soil surface. Volatilization rates for 2,4-D

beneath the soil surface are expected to be even slower, decreasing rapidly with increasing soil depth (Lyman et al. 1982).

As stated above, the n-butyl ester of 2,4-D readily hydrolyzes to the parent acid under environmental conditions. However, the n-butyl ester also readily volatilizes from surface water and soil. No other information on the fate of the esters of 2,4-D could be found in the literature (Zepp et al. 1975).

6.1.3.2 Sorption and Leaching Potential

The pK_a value for 2,4-D is 2.80. Because the pH of most soils is greater than 4.5 and that of most natural waters is greater than 6.0 (Tinsley 1979; Stumm and Morgan 1970), 2,4-D will probably exist primarily in the anionic, dissociated form in the environment. Soils and sediments generally have over all negative potentials except at low pH, thus the adsorption of anions such as the 2,4-D anion to soils and sediments will be weak unless the soils and sediments have large anion exchange capacities or are at a low pH. This would help to explain a low mean reported K_{OC} value of 26 for 2,4-D.

Substitution of the mean reported K_{OC} value of 26 into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) of 0.26 to 2.1 for 2,4-D adsorbed to sediments or soils with organic carbon fractions ranging from 0.01 to 0.08, respectively. Because the estimated $K_{S/W}$ values are less than 10 for an assumed K_{OC} value of 26, it is not expected that the ratio of the total mass of adsorbed 2,4-D to dissolved 2,4-D would exceed 0.01 in surface waters for which the mean K_{OC} value of the suspended and bottom sediment is <0.26. The reason is that the ratio of the water mass to the mass of suspended and exposed bottom sediments exceeds 10^3 in most surface waters (USGS 1983). However, in cases where the sediment has a large anion exchange capacity, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment may be important processes for 2,4-D in surface waters.

Substitution of the mean reported K_{OC} value of 26 into equation A-13 gives an estimated soil TLC R_f value of 0.79 for 2,4-D adsorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling

and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), 2,4-D would be expected to be at least moderately mobile (Class 4) in, and to be at least moderately susceptible to leaching from, surface soils with a K_{OC} value of <26 . However, 2,4-D would be expected to be far less mobile in soils with a large anion exchange capacity.

Although several field studies have indicated that 2,4-D is susceptible to moderate leaching, the higher concentrations of the compound in those studies remained in the upper layers of the soil (Bovey and Young 1980). For example, in tests conducted by the U.S. Air Force, 4,000 pounds per acre of Herbicide Orange were applied at a depth of 15 cm in soil plots in Utah. Although 2,4-D residues were detected to a depth of 90 cm after 282 days, more than 90 percent of the residues remained in the top 30 cm of soil (NRCC 1978). Studies by Barnett et al. (1967 as cited in NRCC 1978) on the movement of 2,4-D residues in soil under simulated rainfall showed that most of the 2,4-D remained at a depth of 0 to 8 cm, although some was present at a depth of 8 to 15 cm. Only negligible amounts were detected below 15 cm. The fact that 2,4-D does not appear to be as susceptible to leaching from soils in the studies cited above as would be predicted by a K_{OC} value of <26 may be due to a major contribution to adsorption by anion exchange.

There have been a number of studies on the removal of 2,4-D from soils by surface runoff water, either through leaching or by erosion of soil particulates to which the herbicides are adsorbed (Barnett et al. 1967; Bovey and Young 1980; Lutz et al. 1973; Lawson 1976). Although substantial quantities of the herbicide are often detected in runoff occurring soon after herbicide applications, concentrations rapidly decline in succeeding runoffs. Total losses of herbicide due to runoff over substantial periods of time do not generally account for more than 5 percent of the applied herbicide. For example, although concentrations of 2,4-D in initial runoff from recently sprayed experimental plots in North Carolina were often relatively high (0.3-4.2 ppm), concentrations in succeeding runoffs rapidly declined (Bovey and Young 1980). Total herbicide loss after several runoffs typically accounted for less than 1 percent of the applied herbicide. Nevertheless, substantial quantities of herbicide can be transported by surface runoff from watersheds receiving heavy herbicide spraying and heavy rainfall.

6.1.3.3 Abiotic Transformations

Although some of the esters of 2,4-D are susceptible to rapid hydrolysis in the environment to 2,4-D (SAIC 1981b), 2,4-D itself is unlikely to undergo significant rates of abiotic hydrolysis in the environment due to its lack of functional groups that are readily susceptible to hydrolysis (Lyman et al. 1982).

Phenoxy herbicides such as 2,4-D can undergo several different photo-reactions in water: photo-oxidation of the phenoxy side chain to form chlorophenols; photonucleophilic displacement of Cl by OH to form chlorophenols; or a photo-reductive dechlorination involving the replacement of Cl with H to form phenoxyacetic acid (Crosby 1976; Akermark 1978).

Zepp et al. (1975) estimated the average photolytic half-life of 2,4-D in shallow clear water as follows. The rate of photolysis was assumed to be given by the following equation:

$$\frac{d[C]}{dt} = -k_A \bar{\Phi} [C]$$

Where

k_A = average rate of sunlight absorption
 $\bar{\Phi}$ = quantum yield.

The average rate of sunlight absorption was calculated by integrating sunlight intensity data over a 12-hour period of sunlight for September on a clear day at latitude 34°N. If the quantum yield is assumed to be independent of wave length or is an average value, the rate of photolysis becomes pseudo first order with a half-life given by:

$$t_{1/2} = \ln 2 / k_A \bar{\Phi}$$

Substituting the value of k_A and a reported quantum yield for 2,4-D in water into equation 2-5, it was estimated that the photolytic half-life of 2,4-D in

clear, shallow water in September at latitude 34°N, exposed to 12 hours of unobstructed sunlight, would be 20 days (Zepp et al. 1975). Estimates of half-lives under cloud cover or in deeper water would be much greater.

6.1.3.4 Biodegradation and Persistence in Soil and Water

Several studies have indicated that 2,4-D is susceptible to relatively rapid rates of degradation in both water and soil. Schultz and Herman (1971) determined the persistence of 2,4-D in the water and mud of nine ponds located in Florida, Georgia, and Missouri. The ponds were sprayed with the dimethylamine salt of 2,4-D at the rate of 2, 4, or 8 pounds per acre acid equivalent of 2,4-D. Residues of 2,4-D declined in Florida and Georgia ponds, from maximums of 0.35 and 0.69 mg/l, respectively, observed 3 days after spraying, to less than 0.005 mg/l within 14 and 28 days, respectively, after spraying. 2,4-D residues in the mud of the ponds at these locations never exceeded 0.05 mg/kg and declined to less than 0.005 mg/kg within 56 days after spraying. Residues in Missouri ponds declined from a maximum of 0.63 mg/l to less than 0.005 mg/l within 56 days after spraying. A maximum value of 0.170 mg/kg 2,4-D residue was found in the mud of these ponds, but no 2,4-D residues could be detected in the mud of the ponds past 28 days after spraying. Altom and Stritzke (1973) reported that the average half-life of 2,4-D in three Oklahoma soils was 4 days.

Norris (1966) studied the persistence of 2,4-D in forest floor litter under laboratory conditions. Approximately 85 percent of 2,4-D applied to red alder forest floor litter was decarboxylated within 300 hours.

6.1.3.5 Summary

Based upon the above discussion the following tentative conclusions can be made concerning the most likely behavior of 2,4-D in soil and water:

- o Most esters of 2,4-D are expected to be rapidly hydrolyzed to the parent acid.
- o Based upon theoretical considerations, volatilization is not expected to be an important removal process for 2,4-D in water or on soil.

- o Based upon theoretical considerations, transport by adsorption to suspended sediment and removal by adsorption to bottom sediments are not expected to be important for sediments with low anion exchange capacity but may be important for sediments with large anion exchange capacities.
- o Based upon reported K_{oc} values for 2,4-D, the compound is expected to be mobile in soil and susceptible to leaching. However, the mobility of 2,4-D would be expected to be much lower in soils with large anion exchange capacities. Although monitoring data have indicated that 2,4-D is moderately susceptible to leaching, leaching does not appear to be as an important process for 2,4-D in some soils as was predicted based on the reported K_{oc} value in surface soils. The reason may be due to possibly strong anion exchange capacities of subsurface soils.
- o Based upon theoretical considerations, 2,4-D is unlikely to undergo significant rates of hydrolysis in the environment. However, 2,4-D does appear to be susceptible to direct photolysis and photooxidation in the environment. A daytime photolysis half-life of 20 days has been estimated for 2,4-D in shallow water in September at latitude 34°N.
- o Based on several studies, 2,4-D appears to be susceptible to almost complete biodegradation within 2 to 8 weeks in soil and surface water.

6.2 OCCURRENCE IN THE ENVIRONMENT

6.2.1 Water

The following section presents the available data from monitoring studies and surveys to determine the extent of occurrence of 2,4-D in public drinking water supplies and water other than drinking water.

6.2.1.1 Occurrence in Drinking Water

Studies at both the national and regional levels have addressed concentrations of 2,4-D in drinking water. The results of three national studies and two regional studies are discussed in this section. Reported levels of 2,4-D in drinking water obtained from groundwater sources and surface water sources are discussed separately.

Ground Water Sources -- National Studies

A detailed survey of the contaminants in the water supplies of 10 cities (selected on the basis of their source of raw water) was conducted as part of the National Organics Reconnaissance Survey (NORS) (USEPA 1975b). Two of the systems sampled, located in Florida and Arizona and serving more than 100,000 individuals, used ground water as their water source. Water samples taken from these water supplies had concentrations of 2,4-D below the minimum quantifiable concentration, although the minimum quantifiable concentration was not reported.

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) was conducted from June 1977 to March 1981. Samples of finished drinking water were collected from 12 ground water systems of varying sizes throughout the United States and analyzed for 2,4-D. None of the drinking water samples from the 12 ground water systems contained levels of 2,4-D in excess of the quantification limit of 0.5 ug/l.

As part of the 1978 Rural Water Survey (USEPA 1984i), samples were collected from 267 households in rural locations throughout the United States for 2,4-D analyses. A total of 71 public ground water systems of varying sizes were covered by the survey. None of the samples collected from these public ground water systems contained concentrations of 2,4-D in excess of the minimum quantification limit of 0.01 ug/l.

Information provided by the Federal Reporting Data System (FRDS 1984), which contains information on public water supplies that are found to be in violation of current Maximum Contaminant Levels (MCLs), indicated that no violations of the 2,4-D MCL of 100 ug/l were reported during the years 1979-1983.

Ground Water Sources -- Regional Study

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. Analysis of samples of finished drinking water taken from 100 water supplies utilizing five aquifers in Florida identified four supplies with positive values of 2,4-D of 0.02 to 0.28 ug/l, well below the MCL of 100 ug/l.

Surface Water Sources -- National Studies

In the NORS survey of 10 cities (USEPA 1975b), samples of drinking water were collected from eight systems having surface waters affected by different types of pollution. The systems were selected based on the type of pollution affecting their water supplies: 1) uncontaminated upland waters; 2) raw water contaminated with agricultural runoff; 3) raw water contaminated with municipal wastes; and 4) raw water contaminated with industrial discharges. Samples of water from one system contaminated with agricultural runoff contained detectable levels of 2,4-D (0.04 ug/l). The minimum quantifiable concentration was not reported.

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) also contained information on levels of 2,4-D in drinking water obtained from surface water sources. Between June 1977 and March 1981, finished drinking water samples were collected from 105 surface water systems of varying sizes throughout the United States and analyzed for 2,4-D. Only one of the 105 surface water systems sampled contained 2,4-D in excess of the quantification limit of 0.5 ug/l. This system was located in Texas, and contained 1.1 ug/l of 2,4-D.

The 1978 Rural Water Survey (USEPA 1984i) also presented data on levels of 2,4-D in drinking water obtained from surface water sources. Samples were collected from 21 public surface water systems of varying sizes and analyzed for 2,4-D. None of the samples collected from these systems contained concentrations of 2,4-D in excess of the minimum quantification limit of 0.01 ug/l.

Drinking water from surface water supplies in the United States must be monitored for 2,4-D at least once every 3 years in accordance with the National Interim Primary Drinking Water Regulations. Data obtained from the FRDS for the period from 1979 to 1983 indicated that no violations of the 2,4-D MCL of 100 ug/l had been reported (FRDS 1984).

Surface Water Sources -- Regional Studies

Irwin and Healy (1978) summarized data collected during a water quality reconnaissance of public water supplies in Florida and reported that finished drinking water samples collected from 9 of 16 surface water supplies contained 2,4-D in the range of 0.04 to 0.94 ug/l, well below the MCL of 100 ug/l.

In a study on the effects of forest runoff on the quality of a public water supply in Oregon, Elliott (1979) observed an ambient concentration of 2,4-D of 50 ug/l.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October, 1984 through August, 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including 2,4-D, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

6.2.1.2 Occurrence in Water Other Than Drinking Water

One national study and six regional studies presented data on monitored levels of 2,4-D in water other than drinking water. All seven studies addressed levels of 2,4-D in surface water.

National Study

The National Surface Water Monitoring Program (NWMP) (1982) presented data on levels of 2,4-D in surface water samples collected throughout the United States during the years 1975-1978. During this period, 1,557 surface water samples were collected and analyzed. Although no detection limit was reported for 2,4-D, 26 samples contained concentrations of 2,4-D ranging up to 1.91 ug/l.

Regional Studies

Truhlar and Reed (1976) reported on water samples collected from four streams in Pennsylvania and analyzed for chlorinated hydrocarbon pesticides during the period from April 1970 to February 1971. The streams drained four different types of land use areas: forest, general farms, orchards, and residential areas. Of the 19 samples collected and analyzed, 10 contained concentrations of 2,4-D in excess of the detection limit. Two-thirds of the samples collected from the stream draining the residential area and half of the samples collected from the streams draining the general farms and orchard areas contained residues of 2,4-D at levels ranging from 0.0 to 0.08 ug/l. No detection limit was reported for the study.

Joyce and Sikka (1977) conducted a study for the U.S. Corps of Engineers to determine the levels of 2,4-D in St. Johns River water as a result of 2,4-D use during routine water hyacinth control operations. A total of 45 water samples were collected from nine locations on the St. Johns River from July 1975 to January 1976. Concentrations of 2,4-D ranging from "non-detectable" to 1.3 ug/l were reported, with an average concentration of 0.17 ug/l (no detection limit was reported).

Barks (1978) presented the results of a USGS water quality study conducted from April 1973 to July 1974 in the Ozark National Scenic Riverways, Missouri. During the study, 20 surface water samples were collected from three sites on the Current River and one site on Jacks Fork. Analysis of unfiltered samples showed a concentration of 2,4-D of 0.03 ug/l in a sample collected on the Current River below Montauk State Park during a storm. No detection limit was reported.

Englande et al. (1973) presented the results of extensive chemical analysis of six Advance Wastewater Treatment (AWT) plant effluents. Four of the sampled plants were located in California, and one each in the District of Columbia and Texas. Although none of the 63 AWT effluent samples contained concentrations of 2,4-D in excess of the 2,4-D MCL of 100 ug/l, mean concentrations of less than 0.023 ug/l and 0.095 ug/l were detected in two effluent samples from two California plants. A mean concentration of less than 0.032 ug/l was detected in samples from the Texas plant. 2,4-D was not detected in the other systems sampled. The number of positive samples and the detection limit were not reported.

Wall et al. (1978) conducted a study in November 1973 to determine the levels of selected herbicides in filtered stream water samples from the Maumee River Basin in northwestern Ohio. Water samples were collected from three rivers in the Maumee River Basin. None of the samples contained concentrations of 2,4-D in excess of the detection limit of 1 ug/l. The number of samples was not reported.

Hiatt (1976, as cited in NAS 1977) detected concentrations of 2,4-D as high as 70 ug/l in samples collected from streams in Oregon after aerial application of the pesticide to forestland. The number of samples analyzed and the detection limit were not reported.

6.2.2 Ambient Air

Stanley et al. (1971, as cited in Grover et al. 1976) and Compton et al. (1972, *ibid.*) reported the results of studies that assessed 2,4-D ambient air levels in 16 U.S. cities over a 1-year period. Two of the three positive

samples reported were from cities in New York (0.00115 and 0.00154 ug/m³) and the third positive sample was from a city in Utah (0.004 ug/m³).

6.2.3 Soil/Sediments

Several studies were identified that examined the occurrence of 2,4-D in soils and sediments. Britton et al. (1983) reported on levels of pesticides in water-sediment mixtures (unfiltered samples) and in bottom material samples collected by the National Stream Quality Accounting Network (NASQAN) in 1976. Throughout the United States, 151 permanent stations plus stations added as part of local programs were sampled for pesticides, including 2,4-D. Water-sediment mixtures were collected quarterly; bottom materials were collected semiannually. 2,4-D was detected in water-sediment samples at one of 14 stations in the Ohio region, four of 12 stations in the Lower Mississippi region, three of 10 stations in the Arkansas-White-Red region, five of 13 stations in the Texas-Gulf region, two of five stations in the Lower Colorado region, and two of six stations in the California region. The maximum level of 2,4-D found at these stations was 1.6 ug/l. No samples of bottom materials contained detectable levels of 2,4-D. The detection limit for 2,4-D in the water-sediment and the bottom material samples was not reported.

The National Surface Water Monitoring Program (NWMP 1982) presented data on levels of 2,4-D in sediment samples collected between 1975 and 1979. Of 542 sediment samples analyzed during that period, only one sample contained a detectable concentration of 2,4-D, at 14.88 ug/kg (collected during the spring of 1978). No detection limit for 2,4-D was reported.

Wall et al. (1978) conducted a study in November 1973 to determine the levels of selected herbicides in bottom sediment material samples from the Maumee River Basin in northwestern Ohio. A total of 21 bottom sediment samples were collected at 6 sites on 3 rivers in the Maumee River Basin. Concentrations of 2,4-D ranging from less than 5 to 90 ug/kg were detected in unconsolidated bottom sediment samples. The detection limit and the number of positive samples were not reported.

6.2.4 Food

The data on levels of 2,4-D in foods were obtained primarily from studies conducted throughout the 1970's. Sources of information on 2,4-D in foods include FDA market basket surveys and other FDA compliance program reports.

Data are limited on the dietary intake of 2,4-D in the United States. Dietary exposure to 2,4-D appears to be low; there have been no findings of 2,4-D in FDA adult market basket surveys since 1973. The average total daily intake of 2,4-D, based on detectable levels of 2,4-D in market basket studies performed between 1965 and 1973, were calculated to range from 0.0006 to 0.07 ug/kg/day (FDA 1981b).

For the period June 1970 to April 1971, residues of 2,4-D ranging from 10 to 130 ug/kg were detected in three leafy vegetable samples. In addition, one residue of 10 ug/kg was identified in leafy vegetable samples taken during the period June 1971 to July 1972. A residue of 2,4-D of 14 ug/kg was detected in a potato sample collected during the period August 1972 to July 1973 (Johnson and Manske 1976; Manske and Corneliussen 1974; Manske and Johnson 1975).

Johnson et al. (1981a) presented data on residues of 2,4-D in infant and toddler foods for the period August 1975 to July 1976. During the infant/toddler studies, 2,4-D was detected in one of the toddler diet samples. None of the infant food samples contained concentrations of 2,4-D in excess of the approximate quantitation limit of 20 ug/kg.

The FDA has also monitored 2,4-D (primarily in small grains) as part of its surveillance and compliance program (FDA 1981b). Sampling results from 1978 to 1982 indicated that only 20 percent of the samples analyzed showed levels of 2,4-D. Concentrations ranged from trace quantities to 2.1 ppm.

It is expected that dietary levels of 2,4-D vary somewhat with geographical location, with higher levels occurring in foods from areas of the sources of 2,4-D exposure. However, because of insufficient data, no estimates could be made of variations in intake by geographical region.

6.3 EXPOSURE SUMMARY

Several comprehensive studies exist that provide data on the extent of occurrence of 2,4-D in drinking water and food. Data on 2,4-D in air are more limited. According to monitoring data collected as part of various Federal surveys conducted from 1975 to 1983, no public water supplies contained 2,4-D at levels exceeding the current Maximum Contaminant Level (MCL) of 100 ug/l. Indeed, of the three Federal surveys reviewed, 2,4-D was detected in only two out of over 200 groundwater and surface water supplies (less than 1 percent) at concentrations of 0.04 ug/l and 1.1 ug/l. Similarly, levels of 2,4-D reported in regional surveys were also low, with concentrations ranging from 0.02 to 0.94 ug/l. These levels are low considering 2,4-D's relatively extensive use in weed control, as well as use on food crops.

Data are limited on the dietary intake of 2,4-D in the United States. Information on 2,4-D in foods is available through FDA market basket surveys and FDA compliance program reports, both of which comprehensively analyze the various classes of food products. The data on levels of 2,4-D in foods were obtained primarily from studies conducted throughout the 1970s. The average total daily intake of 2,4-D, based on detectable levels of 2,4-D in market basket studies performed between 1965 and 1973, ranged from 0.04 to 5.0 ug/day. There have been no findings of 2,4-D in FDA adult market basket surveys since 1973.

Currently available information on the occurrence of 2,4-D is insufficient to determine the national distribution of intake by any of the three routes. The table below indicates that food exposure can result in higher intakes than air or water and that the total non-drinking water intake will be on the order of a few ug/day. The number of people who actually receive such exposures is unknown. EPA has little information on present levels of 2,4-D in ambient and indoor air and in food; therefore, the intakes by these routes cannot be determined with any certainty.

Table 1. Exposure Estimates for 2,4-D

Source	Reported Exposure Levels (low-high)	Estimated Adult Intake
Drinking Water	0 - 1.1 ug/l	0 - 2.2 ug/day
Diet	--	0.04 - 5 ug/day
Air	0 - 0.004 ug/m ³	0 - 0.8 ug/day

7. EDB

7.0 SUMMARY

EDB is a highly volatile liquid that until recently has been used as a soil fumigant and insecticide. EDB is a contaminant of groundwater in areas where it is used agriculturally. It has been found in private drinking water supplies at levels up to several hundred ug/l. Due to the recent cancellation of EDB uses, occurrences of EDB in air, food, and water are expected to decline in the future.

7.1 GENERAL CHARACTERISTICS

7.1.1 Physical/Chemical Properties

1,2-Dibromoethane (ethylene dibromide-EDB) is a colorless liquid at 25°C (Verschuere 1983). Trade names for products containing EDB include Bromofume, Celmide, Dowfume, EDB-85, E-D-Bee, KopFume, Nephis, and EDB (Berg 1986). It has a molecular weight of 187.9, a molecular formula of $C_2H_2Br_2$, a melting point of 9.97°C, and a boiling point of 131.6°C. The aqueous solubility and vapor pressure of EDB at 30°C are 4,310 mg/l (2.3×10^{-3} mol/l) and 17 torr (2.2×10^{-2} atm·m³/mol), respectively (Verschuere 1983).

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant for EDB at 30°C of 9.6×10^{-3} atm·m³/mol (3.9×10^{-3} torr·l/mg). The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant at 30°C for EDB of 0.39. Reported K_{OC} values for EDB range from 36 to 158 (Cohen et al. 1984).

EDB is stable when stored at room temperature, but hydrolyzes in the presence of heat and moisture to hydrobromic acid and ethylene glycol. The rate of this degradation is variable, depending on pH, temperature, and the microbiological populations present (FDA 1981b).

7.1.2 Use

Annual domestic production of EDB was reported by EPA to exceed 280 million pounds. More than 90 percent of the total quantity used, or 260 million pounds of EDB, was estimated to be used as an additive in leaded gasoline, while more than 20 million pounds was used for agricultural purposes (USEPA 1984a). EPA estimated in 1983 that 23 million pounds of EDB were applied to 1.0 million acres of farmland annually as a soil fumigant alone (USEPA 1983c). Soil fumigant use accounted for over 90 percent of total domestic agricultural use of EDB in 1978, and use as a soil fumigant had increased significantly between 1978 and 1983. In 1984-1985, use of EDB decreased to 500,000 pounds due to cancellation of most uses (Kuch 1986). The use of EDB as an additive in gasoline is declining as a result of EPA's regulations phasing out leaded gasoline (USEPA 1983c).

EDB was used in the production of soybeans, cotton, peanuts, pineapples, and 30 other fruit and vegetable crops for protection from attack by nematodes and tropical fruit flies (USEPA 1984a). EDB is used in the fumigation of imported fruit and grain, and spot fumigation of grain milling machinery (USEPA 1983c).

Other minor uses of EDB included application to felled logs, termite control, beehive supers and honeycombs, storage vault fumigation, and the fumigation of bench soil, balled plants, and grass sod to control the Japanese beetle under the Japanese Beetle Domestic Quarantine Program (USEPA 1984a). Major geographic areas where EDB is used include the Southeast and California.

On September 28, 1983, EPA issued a notice of intent to cancel the major uses of EDB. This action was initiated on the basis of the potential oncogenic, mutagenic, and reproductive effects of EDB. Uses of EDB for soil fumigation, fumigation of stored grain, spot fumigation of grain milling machinery, and fumigation of felled logs were scheduled for cancellation within 30 days of the notice. Cancellation of EDB use for quarantine fumigation was scheduled for September 1, 1984 (48 FR 46234). In addition, an emergency suspension order for the use of EDB for soil fumigation was made effective on September 28, 1983 (48 FR 46228). EPA continued registrations of EDB products used for termite control, fumigation of beehive supers, honey

combs, vault fumigation, and Japanese beetle control, with the stipulation that specified changes were made on labels to reduce the level of risk resulting from use (48 FR 46234).

As a result of the cancellation of the majority of uses of EDB, it is expected that the releases of EDB to air and groundwater from agricultural uses will be greatly reduced. While release of EDB to the atmosphere from the use of leaded gasoline can contribute significant airborne concentrations of EDB, these levels are also expected to decrease slowly over the course of the next 10 years as the use of leaded gasoline declines.

7.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of EDB is divided into the following subsections: 7.1.3.1 Volatilization; 7.1.3.2 Sorption and Leaching Potential; 7.1.3.3 Abiotic Transformations; 7.1.3.4 Biodegradation and Persistence in Soil and Water; and 7.1.3.5 Summary. The discussion will emphasize the environmental fate of EDB in soil and water.

7.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as EDB ($H = 9.6 \times 10^{-3}$ atm·m³/mol) with Henry's constants greater than 10⁻⁵ atm·m³/mol are likely to undergo significant rates of volatilization from surface waters under any conditions normally found in the environment. Volatilization half-lives estimated for EDB in rivers or streams and lakes by SAIC using equations A-1 and A-3 through A-8 support this conclusion. Estimated volatilization half-lives for EDB in rivers or streams range from 0.79 hour in a turbulent river or stream 1 m deep to 6.7 days for a stagnant river or stream 10 m deep (see Appendix A). Estimated volatilization half-lives for EDB in turbulent lakes range from 7.4 hours in a lake 1 m deep to 74 hours in a lake 10 m deep.

The rate of volatilization of EDB from ground water to the soil column above is projected to be substantially less than volatilization rates from surface waters to the atmosphere. This is due primarily to the laminar, nonturbulent nature of ground water flow. Transport from ground water by

volatilization may be further reduced by a build-up of chemical in the pore air at the ground water/pore air interface, and an associated decrease in the concentration gradient across the interface.

The use of equation A-9 would be inappropriate for estimating volatilization half-lives for EDB on soils because the equation was derived from data on compounds with vapor pressures several orders of magnitude lower than that of EDB. However, due to a relatively high Henry's constant (9.6×10^{-3} atm·m³/mol) and a relatively low median K_{OC} value of 97, volatilization is probably a significant removal process for EDB on soil.

7.1.3.2 Sorption and Leaching Potential

Substituting the median (97) of the range of reported K_{OC} values from 36 to 158 into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) for EDB ranging from 0.97 to 7.8 for sediments or soils with organic fractions ranging from 0.01 to 0.08. The estimated $K_{S/W}$ values suggest that at equilibrium, the concentration of EDB in suspended and exposed bottom sediment may be several times greater than the concentration in the water column. However, since the estimated $K_{S/W}$ values for EDB are less than 10, it is unlikely that the ratio of the total mass of EDB adsorbed to suspended and exposed bottom sediments to the total mass of EDB dissolved in the water column will exceed 0.01 in most surface waters. The reason is that in most surface waters, most of the time, the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 1,000 (USGS 1983). Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediments are probably not important processes for EDB in surface waters.

Substitution of the median (97) of reported K_{OC} values into equation A-13 gives an estimated soil TLC R_f value (Appendix A) of 0.47 for EDB adsorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), EDB would be expected to have an intermediate mobility (Class 3) in, and be in between being moderately susceptible

and moderately resistant to leaching from, surface soil. EDB has been detected in several samples of ground water from several states (Cohen et al. 1984). In one study, EDB was reported to have leached to a depth of greater than 10 meters under the soil surface (Zalkin et al. 1983, as cited in Cohen et al. 1984).

7.1.3.3 Abiotic Transformations

Johns (1976, as cited in USEPA 1984f) reports a hydrolysis half-life of 5 to 10 days for EDB in neutral aquatic media at ambient temperature. However, preliminary results of another study have led to an estimated hydrolytic half-life for EDB in groundwater of >6 years (Cohen et al. 1984). The discrepancy in hydrolytic half-lives may be due to biologically mediated or enzyme catalyzed hydrolysis reaction in surface water.

There was no information in the literature reviewed by USEPA (1984f) or Cohen et al. (1984) concerning any possible photolytic or oxidative degradation of EDB. However, EDB does not have any chromophores that absorb strongly above 290 nm nor any functional groups susceptible to oxidation. Therefore, EDB is unlikely to undergo significant rates of photolysis or oxidation in the environment.

7.1.3.4 Biodegradation and Persistence in Soil and Water

There is no information in the literature reviewed by USEPA (1984f) or Cohen et al. (1984) concerning the biodegradation of EDB in natural waters and only limited information concerning biodegradation in soils. Castro and Belser (1968, as cited in Cohen et al. 1984) reported that approximate half-lives for EDB in a "bioactive" agricultural soil ranged from 2 to 18 weeks depending only on the soil aliquot used. McKenry and Thomason (1974, as cited in USEPA 1984f) performed a mass balance analysis for EDB in a soil/water system and reported unaccounted for losses of 15 percent after 3 days and 40 percent after 10 days. They attributed the losses to a possible combination of biodegradation, volatilization, and leaching, but did not attempt to determine the relative contributions of each.

7.1.3.5 Summary

Based on the above discussion and the literature reviewed by Cohen et al. (1984) and USEPA (1984f), the following tentative conclusions can be made concerning the behavior of EDB in soil and water:

- o Based primarily on theoretical considerations, volatilization is expected to be the primary removal process for EDB in surface waters and on soils.
- o Based on theoretical considerations and on limited data, transport by adsorption to sediment and removal by adsorption to bottom sediments are not expected to be important processes for EDB in aquatic systems.
- o Based on theoretical considerations and on some leaching and ground water monitoring data, EDB appears to be at least moderately susceptible to leaching from soils.
- o There is a large discrepancy between the reported hydrolytic half-life of 5-10 days in a neutral aquatic medium, and estimated hydrolytic half-lives of >6 years in groundwater. The discrepancy may be due to biological mediation (enzyme catalysis) in the first case.
- o There is no information available concerning any possible photolytic or oxidative degradation of EDB. However, due to its chemical structure, EDB is unlikely to undergo significant rates of photolysis or oxidation in the environment.
- o Estimated degradation half-lives for EDB in the same soil varied from 2 to 18 weeks depending on the soil aliquot, which corresponds to a persistence in soil classification ranging from nonpersistent (half-life <30 days) to persistent (half-life >100 days).
- o Ground water samples from several states have been reported to be contaminated with EDB. However, due to its estimated high rate of volatilization from surface waters, EDB is not expected to significantly contaminate surface water supplies, nor has it been identified in surface water supplies.

7.2 OCCURRENCE IN THE ENVIRONMENT

7.2.1 Water

The following section presents the data available from monitoring studies and surveys to determine the extent of occurrence of EDB in public drinking water supplies and water other than drinking water.

7.2.1.1 Occurrence in Drinking Water

No studies were identified that addressed EDB levels in drinking water from surface water sources; however, several regional studies have addressed levels of EDB in drinking water from ground water sources. Ground water samples were collected between 1980 and 1983 by a number of California State agencies with the assistance of EPA. Concentrations of EDB were detected in samples of water from two small community drinking water supplies in the San Joaquin Valley area. The number of drinking water supplies sampled, the number of samples collected, values for the positive systems, and the detection limit were not reported (USEPA 1983c).

As a result of positive findings in California, EPA requested that the State of Hawaii perform EDB monitoring. Samples of drinking water from more than 100 wells located near areas of EDB use in Hawaii were collected between June and September 1983 (Wong et al. in progress, as cited in USEPA 1983c). Samples of water from four wells at one site contained levels of EDB ranging from 0.02 to 0.10 ug/l. No detection limit for the study was reported.

SAIC/JRB Associates (1981a) identified locations in the United States where organic chemicals were found in groundwater supplies. Levels of EDB ranging from 0.02 to 560 ug/l were detected in 25 samples of water collected from wells in several counties in New Jersey. The total number of samples and the detection limit were not provided. It is not possible to determine the source of the high values from the information presented.

The State of Connecticut began a well water testing program (Chemical Regulation Reporter 1984) in early February 1984, after EDB residues were found in grain and citrus products throughout the United States, as well as in Florida drinking water. Wells located near present or former tobacco fields where EDB had been used until 1982 were tested. A total of 240 public and private wells were sampled. The analysis showed that 32 wells in north central Connecticut contained levels of EDB ranging from 0.1 to 1.4 ug/l. The detection limit was not reported.

7.2.1.2 Occurrence in Water Other Than Drinking Water

Several studies have reported levels of EDB in ground water and surface water other than drinking water. Levels in ground water and surface water are discussed separately below.

Ground Water Sources

The primary sources of information on levels of EDB in groundwater are state surveys conducted to determine whether there is any correlation between EDB use and ground water contamination by EDB. Five states (South Carolina, Florida, Georgia, California, and Washington) have detected EDB in ground water in the range of 0.05 to 20 ug/l (Cohen et al. 1984). In water samples collected from 19 wells in South Carolina, samples from three wells contained levels of EDB ranging from 0.036 to 0.24 ug/l (Senn 1983, as cited in Cohen et al. 1984).

In Florida, water samples have been collected from 334 wells since mid-1983 by the State. Analysis showed that samples of water from 86 of the 334 wells contained EDB concentrations in excess of the detection limit of 0.02 ug/l; 75 of the 86 positive samples contained concentrations greater than 0.1 ug/l (Bigler 1983, as cited in USEPA 1983c).

As a result of notification to EPA by EDB registrants that levels of EDB were as high as 100 ug/l in three wells sampled in Georgia, further monitoring of the wells in the area was initiated by EPA and the U.S. Geological Survey. Analysis showed that samples of water from 6 out of 19 wells were contaminated with EDB in the range of 0.03 to 11.8 ug/l (Jovanovich and Cohen in review as cited in USEPA 1983c).

A California study conducted in 1980 found that samples of ground water from 2 out of more than 200 wells sampled were contaminated by EDB. The two positive samples contained 0.1 and 0.2 ug/l EDB (Zalkin et al. in progress, as cited in USEPA 1983c). Additional ground water monitoring detected EDB in 15 to 20 samples of more than 250 water samples analyzed. The typical values of the positive samples ranged from 0.1 to 2.0 ug/l EDB (USEPA 1983c). With the exception of the Florida survey, no detection limit for EDB was reported for these state surveys.

The Washington Department of Agriculture, in cooperation with the Department of Social and Health Services (DSHS) and local health departments, conducted a study of ground water in five western Washington counties for EDB contamination (Washington State Department of Social and Health Services 1985). Shallow and deep wells of 95 public and private drinking water supplies were sampled from June to October 1984. Private wells were chosen if sampling would provide information to protect the public. Sample analysis was performed by the U.S. Environmental Protection Agency, Region X Laboratory. In four counties, a total of 13 supplies (10 public, 3 private) were contaminated with EDB above the health advisory level of 0.02 ug/l, with a population served of approximately 550 persons. Out of a total of 131 samples analyzed (including an unspecified number of blanks), 34 were positive for EDB with a mean concentration of 0.76 ug/l (range = 0.018 to 5.7 ug/l). The detection limit was 0.01 ug/l.

Surface Water Sources

One sample of surface water was collected from an agricultural area in Georgia that had been treated with EDB. The sample did not contain EDB in excess of the detection limit, although the detection limit was not reported (Jovanovich and Cohen in review, as cited in USEPA 1983c).

Five samples of rainfall and runoff water collected near an EDB fumigation center in Florida contained 0.9-2.0 ug/l EDB (Going and Spigarelli 1976, as cited in Brodzinsky and Singh 1982).

7.2.2 Ambient Air

Brodzinsky and Singh (1982) compiled data on levels of EDB in ambient air from published and unpublished sources into a master file. They analyzed and assessed data quality, reliability, and representativeness. Quality codes were assigned based on a quantitative assessment or on the authors' best professional judgment. Concentrations ranged from "undetectable" in clean atmospheres to 240 ug/m³. In urban areas, typical EDB concentrations ranged from 0.08 to .460 ug/m³. Using data with quality codes of excellent, good, or acceptable, the authors calculated the following median EDB concentrations: rural/urban areas, 0.0 ug/m³; urban/suburban areas, 0.2 ug/m³; and source-dominated areas (undefined), 1.5 ug/m³.

Due to the decline of the use of EDB in gasoline and EPA's cancellation of the use of EDB as a soil, grain, and quarantine (fruit and vegetable) fumigant, current ambient air levels of EDB are expected to be lower than the levels in the above study.

7.2.3 Soil/Sediments

Very little information was available on studies that examined EDB occurrence in soil and sediments. Only one soil study was identified, which involved soil sample collection near an agricultural fumigation center in the State of Florida. Analysis results indicated low levels of EDB (0.4 to 3.4 ug/kg) in the soil samples. No detection limit was reported (Going and Spigarelli 1976, as cited in Brodzinsky and Singh 1982).

7.2.4 Food

The dietary intake of EDB in the United States was estimated by EPA in Position Documents 2/3 and 4 and in two technical support documents (USEPA 1983c, 1984c,f). Dietary intakes were calculated for the following uses of EDB: soil fumigation, post-harvest fumigation of grain and grain milling machinery, and quarantine fumigation of citrus and tropical fruits. Total intake estimates of EDB resulting from these uses for the U.S. population generally ranged between <0.01 and 0.18 ug/kg/day.

Dietary levels of EDB may vary with geographic location (see Table 7-1 below). The highest dietary intakes were estimated to occur in the South, where the combined intake of EDB from citrus and grain totals 0.0062 ug/kg/day (USEPA 1984b,c).

Most of the information identified on the occurrence of EDB in foods in the United States was from studies that monitored EDB residues in grains (USEPA 1983c). USEPA summarized monitoring data for EDB residues in raw grains, uncooked and cooked grain products, and in baby foods in a scientific support and decision document for grain and grain milling fumigation uses (USEPA 1984b).

Table 7-1. Dietary Levels of EDB by Geographic Region

Region	Dietary intake (ug/kg/day)	
	Citrus ^a	Grain ^b
Northeast	0.00052	0.0051
North Central	0.0005	0.0052
South	0.0003	0.0059
West	0.00074	0.0052

a USEPA 1984c

b USEPA 1984b

In raw grains, the highest average residue reported was 2,000 ug/kg in other grains, which includes rice, barley, oats, rye, and sorghum (FDA 1983, as cited in USEPA 1984b). Levels in raw wheat ranged from 4.9 ug/kg (USDA 1984a, as cited in USEPA 1984b) to 43 ug/kg (Grocery Manufacturers of America 1984a,b, as cited in USEPA 1984b). EDB levels in raw corn ranged from not detected (North Carolina Department of Agriculture 1984, as cited in USEPA 1984b) to 220 ug/kg (Grocery Manufacturers of America 1984a,b, as cited in USEPA 1984b). The detection limits and number of positive samples were not presented for any of these studies.

For uncooked grain products, the highest level of EDB detected was 140 ug/kg in corn (Grocery Manufacturers of America 1984a,b, as cited in USEPA 1984b). Levels of EDB in wheat ranged from 2.9 ug/kg (Florida Department of Agriculture 1984, as cited in USEPA 1984b) to 22 ug/kg (MRI 1984, as cited in USEPA 1984). EDB concentrations in other grains ranged from 0.75 ug/kg (Georgia Department of Agriculture 1984, as cited in USEPA 1984b) to 2.3 ug/kg (North Carolina Department of Agriculture 1984, as cited in USEPA 1984b).

Cooked grain products had the overall lowest EDB concentrations. The highest concentration was 7.7 ug/kg in wheat (North Carolina Department of Agriculture 1984, as cited in USEPA 1984b). The highest reported level in cooked corn was 4.7 ug/kg (MRI 1984, as cited in USEPA 1984b).

Of 86 baby foods sampled, only two were positive for EDB. These were in wheat and rice with a range of <1-1.3 and <1-1.5 ug/kg, respectively (Grocery Manufacturers of America 1984b, as cited in USEPA 1984b).

Wallace et al. (1984) reported results from the Total Exposure Assessment Methodology (TEAM) survey analysis for EDB in composite samples of selected FDA food classes. The food classes chosen for the studies (dairy, meat, fatty food, and beverages) were those expected to contain detectable levels of volatile organic chemicals. EDB was not quantified in any of the composite samples analyzed.

Monitoring data for EDB in citrus was submitted to EPA from numerous sources (USEPA 1984f). In all, EDB residues in 450 samples of whole citrus fruit and 130 samples of citrus pulp have been determined. EDB residues in whole fruit ranged from "not detected" (<1 ug/kg) to 16,000 ug/kg, with a median of 250 ug/kg and an average of 1,633 ug/kg. Residues of EDB in citrus pulp ranged from <1 ug/kg to 6,250 ug/kg, with a median of 265 ug/kg and an average of 373 ug/kg.

These estimates reflect uses of EDB (soil and fruit fumigation) which have been cancelled or greatly reduced. Because of these restrictions, current intakes are expected to be less than the above estimates.

7.3 EXPOSURE SUMMARY

The data currently available on the occurrence of 1,2-dibromoethane or ethylene dibromide (EDB) in drinking water, air, and food are limited, but suggest low levels of contamination from each route of exposure. EDB, a highly volatile liquid that was used until recently as an agricultural fumigant, has been detected as a contaminant of ground water supplies in agricultural areas. Its use as an additive to leaded gasoline has also produced contamination of ambient air, especially in urban districts. Due to the 1983 cancellation of agricultural uses and to a decline in the use of leaded gasoline, EDB occurrence in each medium is expected to decline.

The detection of EDB at levels ranging from 0-20 ug/l in drinking water studies conducted in various regions of the United States indicates the potential for exposure in agricultural areas where EDB use was more extensive. Because EDB does not tend to bind to soils, it is readily available for leaching into ground water supplies. It is susceptible to volatilization from surface soils and thus to contamination of ambient air in agricultural areas. EDB's use in gasoline also provides a source for contamination of ground water supplies in urban areas through the leaking of gasoline storage tanks and the leaching of the compounds. The volatilization of EDB from gasoline uses provides a significant release of this pollutant to air in urban areas where a greater number of automobiles and gasoline engines can be found. Ambient air concentrations range from "undetectable" to 240 ug/m³, with typical levels in urban/suburban areas of 0.20 ug/m³. However, EDB releases from gasoline emissions are expected to be decreasing as a result of decreasing use of EDB in gasoline.

The estimated daily intakes from food were derived from dietary levels presented in EPA's Position Document 2/3, Position Document 4, and two technical support documents (USEPA 1983c, 1984b,c). These intake levels were calculated from results of studies conducted by EPA to evaluate the use of EDB as a soil fumigant, a post-harvest fumigant of grain, a fumigant of grain milling machinery, and a quarantine fumigant of citrus and tropical fruits. As indicated before, current levels are expected to be lower than this estimate. Results are summarized in Table 7-2.

Table 7-2. EXPOSURE ESTIMATES FOR EDB

Source	Reported Exposure Levels (low to high)	Estimated Adult Intake
Drinking Water	0 - 20 ug/l	0 - 40 ug/day
Diet	--	<0.05 ug/day
Air	0 - 0.20 ug/l	0 - 4 ug/day

The information currently available on the occurrence of EDB in the environment and the potential for exposure is insufficient to determine the distribution

of exposure on a national scale from any of the three sources. The estimated daily intake levels provided in the above table suggest that similar ranges of intake occur from ambient air and drinking water, and that the potential for intake from consumption of foods is very small.

However, the number of people who are actually exposed to such high exposure levels from food or air sources is unknown. Because the ranges of possible exposure and intake levels from all three sources are so wide and the available data do not reflect recent declines in uses, an attempt to provide a combined or cumulative daily intake estimate should not be made at this time.

8. HEPTACHLOR/HEPTACHLOR EPOXIDE

8.0 SUMMARY

Heptachlor is an insecticide that was extensively used prior to 1974. EPA has limited the use of heptachlor to subterranean termite control. The current use of heptachlor continues to provide a low-intensity threat of contamination.

8.1 GENERAL CHARACTERISTICS

8.1.1 Physical/Chemical Properties

Heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) is a cyclodiene insecticide (NAS 1977). Synonyms and identifiers for heptachlor include Drinox H-34®, Gold Crest H-60, Heptamul®, and Heptox (Berg 1986). Termide, a mixture of heptachlor and chlordane, is a termiticide (USEPA 1983b).

Heptachlor is a white crystalline substance at 25°C. It has a molecular weight of 373.75, a molecular formula of $C_{10}H_5Cl_7$, and a melting point of 95-96°C (Windholz 1976). The aqueous solubility and vapor pressure of heptachlor at 25°C are 0.18 mg/l (4.8×10^{-7} mol/l) and 3.0×10^{-4} torr (3.9×10^{-7} atm), respectively (Mabey et al. 1981).

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant for heptachlor at 25°C of 8.1×10^{-4} atm·m³/mol. The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant for heptachlor at 25°C of 0.033. Heptachlor has an estimated K_{oc} value of 1.2×10^4 (Mabey et al. 1981).

Heptachlor epoxide is a biodegradation product of heptachlor that is frequently detected in areas of heptachlor use. It has a molecular weight of 389.2, a molecular formula of $C_{10}H_5Cl_7O$, and a melting point of 157-160°C (Mabey et al. 1981; Callahan et al. 1979). At 25°C, heptachlor epoxide has an aqueous solubility of 0.36 mg/l (9.0×10^{-7} mol/l) and a vapor pressure of 3.0×10^{-4} torr (3.9×10^{-7} atm) (Mabey et al. 1981).

The ratio of the vapor pressure to the aqueous solubility gives an estimated Henry's constant for heptachlor epoxide at 25°C of 4.3×10^{-4} atm·m³/mol. The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant for heptachlor epoxide at 25°C of 0.018. Heptachlor epoxide has an estimated K_{OC} value of 2.2×10^2 (Mabey et al. 1981).

8.1.2 Use

Prior to 1974, heptachlor was widely used as a pre-emergent insecticide for the control of corn rootworms, wireworms, and cutworms; as a seed treatment; as a soil treatment for the control of termites and ants; and on gardens, lawns, turf, and ornamentals (USEPA 1976). In 1974, EPA issued a notice of intent limiting registered uses of heptachlor to subsurface control of termites and dipping of roots and tops of nonfood plants. In 1975, the EPA Administrator issued a notice of intent to suspend the registrations of certain pesticide products containing heptachlor (USEPA 1983b).

On March 6, 1978, EPA issued a final cancellation order putting into effect the terms of settlement for the cancellation proceedings (USEPA 1983b). Under this cancellation order, an agreement was outlined to phase out the nontermite uses of heptachlor over a 5-year period. All uses permitted during the phase-out period were restricted to treatment by certified applicators or professional commercial seed treatment companies.

Currently, heptachlor is used to control subterranean termites. Between 0.75 and 1 million pounds of heptachlor were used in 1986 (Kuch 1986). Heptachlor has limited use as a single active ingredient and usually is applied in combination with chlordane (USEPA 1983b). A second approved use of heptachlor is to control fire ants in sugarcane and pineapple fields in Hawaii.

Approximately 30 percent (or 550,000 pounds) of the heptachlor used in 1971 was applied to commercial and residential structures for protection against termites and to nurseries, lawns, and gardens. By 1974, domestic use of heptachlor for termite control had increased to 1.4 million pounds (USEPA 1976). In 1983, between 1 and 2 million pounds of heptachlor were used in the United States for termite control (USEPA 1983b).

Heptachlor is present as an impurity in chlordane; typically, heptachlor constitutes 10 percent of technical grade chlordane (USEPA 1980f). Nearly 10 million pounds of chlordane were applied in the United States in 1980; approximately 1 million pounds of heptachlor would have been present as an impurity in chlordane in that year. EPA (USEPA 1983b) reported that the largest quantity of chlordane was initially distributed to EPA Region IV, which includes Alabama, Georgia, Florida, Mississippi, North Carolina, South Carolina, Tennessee, and Kentucky. Because chlordane is applied by subsurface ground injection, the potential for water contamination in some areas may be high.

8.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of heptachlor and heptachlor epoxide is divided into the following subsections: 8.1.3.1 Volatilization; 8.1.3.2 Sorption and Leaching Potential; 8.1.3.3 Abiotic Transformations; 8.1.3.4 Biodegradation and Persistence in Soil and Water; and 8.1.3.5 Summary. The discussion will emphasize the environmental fate in soil and water.

8.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as heptachlor ($H = 8.1 \times 10^{-4} \text{ atm}\cdot\text{m}^3/\text{mol}$) and heptachlor epoxide ($H = 4.3 \times 10^{-4} \text{ atm}\cdot\text{m}^3/\text{mol}$) are likely to undergo significant rates of volatilization from surface waters under any conditions normally found in the environment. Volatilization half-lives for heptachlor and heptachlor epoxide in rivers or streams and in turbulent lakes were estimated by SAIC using equations A-1 and A-3 through A-8 (see Appendix A). The estimated volatilization half-lives indicate that volatilization is probably an important removal process for heptachlor epoxide in virtually all surface waters and for heptachlor in many surface waters. However, in the case of heptachlor, which is much more susceptible than heptachlor epoxide to competing removal processes such as hydrolysis, biodegradation, and adsorption, volatilization may not be an important removal process in some deep and/or stagnant waters. Estimated volatilization half-lives for heptachlor and heptachlor epoxide in rivers or streams range from 2.2 hours and 3.3 hours, respectively, in a turbulent river or stream 1 m deep to 3.3 months and 3.5 months, respectively, in a stagnant river or stream 10 m deep.

Estimated volatilization half-lives for heptachlor and heptachlor epoxide in turbulent lakes range from 13 hours and 16 hours, respectively, in a lake 1 m deep to 5.6 days and 6.8 days, respectively, in a lake 10 m deep.

The volatilization rates of heptachlor and heptachlor epoxide from ground water to the soil column are projected to be substantially less than those from surface waters to the atmosphere. This is due primarily to the laminar (nonturbulent) nature of ground water flow. Volatilization rates from ground water may be further reduced by a build-up of the chemicals in the pore air at the pore air/ground water interface, which would decrease the concentration gradients across the interface.

Substitution of the estimated K_{OC} values of 1.2×10^4 for heptachlor and 2.2×10^2 for heptachlor epoxide (Mabey et al. 1981) into equation A-9 along with the compounds' vapor pressures of 3×10^{-4} torr and aqueous solubilities of 0.18 mg/l and 0.36 mg/l, respectively, gives estimated volatilization half-lives of 2.7 hours and 5.8 minutes for heptachlor and heptachlor epoxide, respectively, adsorbed to the soil surface. Volatilization rates for heptachlor and heptachlor epoxide beneath the soil surface would be much slower, decreasing rapidly with increasing soil depth (Lyman et al. 1982).

8.1.3.2 Sorption and Leaching Potential

Substitution of the estimated K_{OC} values of 1.2×10^4 for heptachlor and 2.2×10^2 for heptachlor epoxide (Mabey et al. 1981) into equation A-11 (see Appendix A) gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) ranging from 1.2×10^2 to 9.6×10^2 for heptachlor and from 2.2 to 9.6 for heptachlor epoxide adsorbed to sediments or soils with organic carbon fractions ranging from 0.01 to 0.08, respectively. The estimated $K_{S/W}$ values indicate that at equilibrium the concentration of heptachlor in suspended and bottom sediment may be several hundred times the concentration in the water column and that the concentration of heptachlor epoxide in suspended and bottom sediment may be several times the concentration in the water column. However, because the estimated $K_{S/W}$ values for heptachlor epoxide are all less than 10, it is unlikely that the ratio of the total mass of heptachlor epoxide adsorbed to suspended and bottom sediment to the total mass of heptachlor epoxide dissolved in the water column will exceed 0.01 in most surface waters.

The reason is that the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 10^3 in most surface waters most of the time (USGS 1983). Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are not expected to be important processes for heptachlor epoxide in surface waters. However, because the estimated $K_{s/w}$ values for heptachlor exceed 100, the ratio of adsorbed to dissolved heptachlor will probably exceed 0.1 in some surface waters, thereby making such processes at least occasionally important for heptachlor.

Substitution of the estimated K_{oc} values of 1.2×10^4 for heptachlor and 2.2×10^2 for heptachlor epoxide into equation A-13 gives estimated soil TLC R_f values (Appendix A) of <0.1 and 0.32 for heptachlor and heptachlor epoxide, respectively, adsorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm^3 . Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties, heptachlor would be expected to be immobile (Class 1) in, and resistant to leaching from, surface soil. Heptachlor epoxide would be expected to be moderately immobile (Class 2) in, and moderately resistant to leaching from, surface soil.

3.1.3.3 Abiotic Transformations

Demayo (1972, as cited in Callahan et al. 1979) has reported a neutral first-order hydrolysis rate constant of $3.0 \times 10^{-2} \text{ hr}^{-1}$ for heptachlor in distilled water at 30°C . Assuming that acid and base catalyzed hydrolysis does not contribute significantly to the overall rate of hydrolysis over the normal pH range of 6-9 in natural waters, substitution of that rate constant into equation A-1 (Appendix A) gives an estimated hydrolysis half-life of 23 hours for heptachlor in natural waters at 30°C . Eichelberger and Lichtenberg (1971, as cited in Callahan et al. 1979) reported a hydrolysis rate for heptachlor in Ohio river water at 25°C that roughly corresponds to a hydrolysis half-life of 3.5 days. They reported that no heptachlor remained 2 weeks after introducing the compound to river water and that the only hydrolysis product identified during that time was 1-hydroxychlorde. However, after 2 weeks, they began to detect heptachlor epoxide, which constituted approximately 40 percent of the initial heptachlor present after 4 weeks. Their work suggests

that heptachlor is hydrolyzed in natural waters to 1-hydroxychlorde-
ne, which is then biologically transformed to heptachlor epoxide. Based on the report
by Eichelberger and Lichtenberg (1971, as cited in Callahan et al. 1979) that
heptachlor epoxide remained stable in Ohio River water for 3 weeks, heptachlor
epoxide appears to be resistant to hydrolysis.

Heptachlor and heptachlor epoxide in organic solvents and as solid films
are susceptible to direct and sensitized photolysis when exposed to light with
wavelengths above the approximate solar radiation cutoff at the earth's surface
of 290 nm. Therefore, both compounds may be susceptible to significant rates
of direct and/or sensitized photolysis in shallow surface waters or on the soil
surface. However, no information is available that would allow estimates to be
made of photolysis rates in water or soil (Callahan et al. 1979).

There are no experimental data available on the photooxidation of hepta-
chlor or heptachlor epoxide in surface waters. However, based on structural-
activity relationships, Mabey et al. (1981) estimate second-order rate constants
of $3 \times 10^{10} \text{ M}^{-1} \text{ hr}^{-1}$ and $2,500 \text{ M}^{-1} \text{ hr}^{-1}$ for the oxidation of heptachlor by
singlet oxygen ($^1\text{O}_2$) and peroxy radicals ($\text{RO}_2^\cdot$), respectively, in natural waters.
The substitution into equation A-15 of those rate constants and assumed concen-
trations of 10^{-12}M and 10^{-9}M for singlet oxygen and peroxy radicals, respectively,
in sunlit natural waters, and substitution of the resulting pseudo first-order
rate constant into equation A-1, gives an estimated photo-oxidation half-life
of 23 hours for heptachlor in sunlit shallow surface waters. This indicates
that photo-oxidation may be competitive with hydrolysis in removing heptachlor
from sunlit, shallow surface waters. However, the estimated second-order rate
constants of $<3,600 \text{ M}^{-1} \text{ hr}^{-1}$ and $20 \text{ M}^{-1} \text{ hr}^{-1}$ for the photo-oxidation of heptachlor
epoxide by $^1\text{O}_2$ and $\text{RO}_2^\cdot$, respectively, indicate that photo-oxidation is probably
not an important process for the removal of heptachlor epoxide.

8.1.3.4 Biodegradation and Persistence in Soil and Water

As discussed earlier, Eichelberger and Lichtenberg (1971, as cited in
Callahan et al. 1979) reported that following the rapid abiotic hydrolysis of
heptachlor to 1-hydroxychlorde-
ne, the 1-hydroxychlorde-
ne was more slowly bio-
transformed over a several-week period to primarily heptachlor epoxide. In

contrast, Lu et al. (1975, as cited in Callahan et al. 1979) studying a model aquatic microcosm concluded that after the rapid abiotic hydrolysis of heptachlor to 1-hydroxychlordene, the 1-hydroxychlordene was rapidly biotransformed to primarily 1-hydroxy-2,3-chlordene epoxide, but that the heptachlor epoxide formed constituted no more than 5 percent of the original heptachlor added.

Miles et al. (1969, as cited in Callahan et al. 1979) reported that soil microorganisms under aerobic conditions converted heptachlor in solution over a several-week period to various metabolic products, including heptachlor epoxide and 1-hydroxy-2,3-chlordene epoxide. Miles et al. (1971 as cited in Callahan et al. 1979) reported that the major metabolic product formed from the anaerobic degradation of heptachlor in solution by soil microorganisms was chlordene.

Rao and Davidson (1980) reported a mean half-life for heptachlor in soils of 63 days under aerobic conditions in the laboratory. However, under field conditions, they reported a much higher mean half-life of 426 days for heptachlor in soils. Heptachlor epoxide is reported to be much more resistant to hydrolysis than heptachlor and to biodegradation than 1-hydroxychlordene and is very persistent in both soil and water (Callahan et al. 1979).

8.1.3.5 Summary

Based on the above discussion and the literature review by Callahan et al. (1979), the following tentative conclusions can be made concerning the most likely behavior of heptachlor and heptachlor epoxide in soil or water:

- o Based on theoretical considerations, volatilization is expected to be an important removal process for heptachlor in shallow, turbulent surface waters and on the soil surface. However, volatilization is not expected to be competitive with the rapid hydrolysis of heptachlor in many deeper and/or stagnant surface waters. Estimated volatilization rates for heptachlor epoxide are comparable to those of heptachlor, but due to the resistance of heptachlor epoxide to hydrolysis and biodegradation, volatilization is expected to be an important removal process for heptachlor epoxide in most surface waters and on soil.
- o Based on theoretical considerations, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are

expected to be important processes for heptachlor in some surface waters, but not for heptachlor epoxide.

- o Based on theoretical considerations, heptachlor is expected to be resistant and heptachlor epoxide moderately resistant to leaching from soils.
- o Heptachlor appears to have an abiotic hydrolysis half-life of about 1 to 3 days in natural waters. The major product of hydrolysis is 1-hydroxychlordene. Heptachlor epoxide appears to be resistant to abiotic hydrolysis and has an estimated hydrolysis half-life exceeding several years in natural waters.
- o Both heptachlor and heptachlor epoxide appear to be susceptible to direct and sensitized photolysis in the environment, but the available information is too limited to estimate rates.
- o Photooxidation primarily by singlet oxygen is expected to be competitive with hydrolysis in sunlit shallow surface waters for heptachlor but not heptachlor epoxide.
- o Following the rapid abiotic hydrolysis of heptachlor to 1-hydroxy chlordene in soil and water, the 1-hydroxychlordene undergoes much slower rates of biotransformation to such products as heptachlor epoxide, 1-hydroxy-2,3-chlordene epoxide, and chlordene. Based on limited data, 1-hydroxy-2,3-chlordene epoxide appears to be the primary metabolic product under aerobic conditions, and chlordene appears to be the primary metabolic product under anaerobic conditions. Heptachlor epoxide is formed under aerobic conditions, but to a far lesser degree than 1-hydroxy-2,3-chlordene epoxide.
- o Heptachlor epoxide appears to be extremely resistant to both hydrolysis and biodegradation and is very persistent in soil and water.

8.2 OCCURRENCE IN THE ENVIRONMENT

8.2.1 Water

The following section presents data available from monitoring studies and surveys to determine the extent of occurrence of heptachlor and its transformation product, heptachlor epoxide, in public drinking water supplies and water other than drinking water.

8.2.1.1 Occurrence in Drinking Water

Several studies at the regional level have addressed concentrations of heptachlor and heptachlor epoxide in drinking water. The results of 10 regional studies are discussed in this section. Where possible, reported levels of heptachlor and heptachlor epoxide in drinking water from ground water sources and surface water sources have been discussed separately.

Ground Water Sources

Twelve towns in Connecticut were sampled during 1984-1985 for heptachlor and heptachlor epoxide by the Connecticut Agricultural Experiment Station, New Haven, Connecticut (Waggoner 1985). These towns, combined, serve a population of over 570,000 people. Drinking water wells were sampled at 42 locations and no samples were positive for either heptachlor or heptachlor epoxide (detection limits were 0.2 ug/l and 0.47 ug/l, respectively).

Shallow drinking water wells of 10 counties in northwest Mississippi were analyzed in 1983-1984 during a Mississippi State University study on pesticide hazard assessment (MSU 1984). No positive samples were found for either heptachlor or heptachlor epoxide out of 143 samples analyzed (detection limit = 0.001 ug/l).

Similarly, no positive results were obtained from 67 samples analyzed in Long Island, New York, for either heptachlor or heptachlor epoxide. These results were from a 1984 study reported by the Suffolk County Department of Health Services (Holden 1986). No detection limit(s) was reported.

Drinking water supplies of the Floridian aquifer were analyzed at 96 locations in 1984 by the Florida Department of Environmental Regulation and the U.S. Geological Survey (Holden 1986). These supplies serve a combined population of over three million people. Less than 8 percent of the samples were positive for any of the pesticides sampled for, including heptachlor and heptachlor epoxide. No other information was reported.

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. None of the 100 water supplies sampled using the 5 aquifers in Florida contained heptachlor and heptachlor epoxide in excess of the detection limits. The detection limits were not reported.

Drinking water wells were sampled in Idaho for heptachlor epoxide by the Idaho Department of Health and Welfare (1984). One sample out of 107 was positive with a concentration of 0.015 ug/l (no detection limit was reported).

Sandhu et al. (1978) summarized the results from a study conducted in two rural counties in South Carolina. Water supplies sampled were outside incorporated municipalities. Samples were taken randomly from wells where there was no pretreatment prior to use. It was not noted whether these supplies were public or private. Also, data were collected on drinking water from different land use areas in each county (i.e., agricultural, forest, and residential). The number of samples taken and the number of positive samples were not reported; however, the percent of samples exceeding the detection limit of 0.01 ug/l was reported by the county.

Results indicated that 62.5 percent of the samples taken in Chesterfield County had detectable levels of heptachlor and 42 percent had detectable levels of heptachlor epoxide. The sample means were 0.015 and 0.008 ug/l for heptachlor and heptachlor epoxide, respectively. In Hampton County, 45.5 percent of the samples contained heptachlor and 64 percent of the samples contained heptachlor epoxide in excess of the detection limit. The sample means for the Hampton County samples were 0.009 and 0.018 ug/l for heptachlor and heptachlor epoxide, respectively. (These percentages included samples taken from forest land use areas.) Concentrations of heptachlor in drinking water samples from agricultural areas in Chesterfield and Hampton counties ranged from not detected to 0.16 ug/l with a mean of <0.01 ug/l (not detected). For heptachlor epoxide, concentrations ranged from not detected to 0.09 ug/l with a mean of <0.01 ug/l (not detected). In residential areas in both counties heptachlor concentrations of heptachlor and heptachlor epoxide in drinking water samples ranged from not detected to 0.045 ug/l and not detected to 0.01 ug/l, respectively. Sample means were <0.01 ug/l (not detected) in all cases.

Tucker and Burke (1978) reported that heptachlor epoxide was detected at a level of 0.6 ug/l in water from a public drinking water supply well in Camden County, New Jersey.

Surface Water Sources

Irwin and Healy (1978) reported that none of 16 surface water supplies sampled in Florida contained heptachlor or heptachlor epoxide in excess of the detection limits. The detection limits were not reported.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including heptachlor and heptachlor epoxide, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

Unspecified Sources

Pellizzari et al. (1979) presented monitoring data on halogenated hydrocarbons in drinking water from the northern New Jersey area and the Buffalo/Niagara, New York area. The limits of detection ranged from 0.005 to 0.025 ug/l for both studies. Of 22 drinking water samples taken from the northern New Jersey area, two samples (9%) contained heptachlor at levels of 0.007 and 0.02 ug/l, and none contained heptachlor epoxide. None of the 16 drinking water samples from the Buffalo/Niagara area were found to contain heptachlor or heptachlor epoxide in excess of the detection limits.

In a report on source identification of pollutants entering a sewage treatment plant, Levins et al. (1979a) sampled two drinking water sources in a drainage basin in Georgia. Although detection limits were not reported, heptachlor and heptachlor epoxide were not detected in either of the drinking water samples.

8.2.1.2 Occurrence in Water Other Than Drinking Water

Three national studies are summarized for the occurrence of heptachlor and heptachlor epoxide in surface waters. Eight regional studies addressed levels of heptachlor and heptachlor epoxide in water other than drinking water. Two of the regional studies addressed levels of heptachlor and heptachlor epoxide in ground water, and six studies provided data on levels of heptachlor and heptachlor epoxide in surface water.

Ground Water Sources

Ground water wells in 25 California counties were analyzed as part of the California State Board's Toxics Special Project during 1984 (Cohen and Bowes 1984). Heptachlor was found in three samples with a maximum concentration of 0.3 ug/l. The other positive values, total number of samples, and detection limit were not reported.

Tucker and Burke (1978) presented data on levels of heptachlor and heptachlor epoxide in samples of water collected from 163 wells, including

private and public drinking water supplies, industrial sites, and wells in the vicinity of landfills in nine New Jersey counties. The analysis showed that samples of water from three supply wells contained heptachlor and samples from seven wells contained heptachlor epoxide in excess of the minimum reportable concentration of 0.01 ug/l. The maximum values for heptachlor and heptachlor epoxide were 1.0 and 0.6 ug/l, respectively. The maximum concentration for heptachlor epoxide occurred in a public drinking water supply well.

Surface Water Sources

National studies of surface water analyses for heptachlor and heptachlor epoxide were conducted by USEPA (1976) and Breidenbach et al. (1967, as cited in USEPA 1980f). The overall mean as reported for both pesticides was 0.0063 ug/l. The minimum values determined for each were both 0.001 ug/l, and the maximum values were 0.035 ug/l and 0.02 ug/l for heptachlor and heptachlor epoxide, respectively. The number of positive values, total number of samples, and detection limit were not reported.

The National Pesticide Monitoring Network examined rivers nationwide from 1975 to 1980 (Gilliom et al. 1985). Heptachlor epoxide was reported as being detected in 9 out of 2,946 samples analyzed from 177 locations (detection limit = 0.01 ug/l). The mean and range of values were not reported.

Heptachlor and heptachlor epoxide were analyzed for in rivers and streams in upstate New York (Estabrooks no date) in 1982-1983. No samples for either pesticide were found to be positive out of 252 samples analyzed. The detection limit was 10.0 ug/l.

Barks (1978) presented the results of a USGS water quality study conducted from April 1973 to July 1974 in the Ozark National Scenic Riverways, Missouri. During the study, 20 surface water samples were collected from 3 sites on the Current River and 1 site on Jacks Fork and analyzed for pesticide content. The analysis of unfiltered samples found no heptachlor or heptachlor epoxide in excess of the detection limit (the detection limit was not reported).

Englande et al. (1978) presented the results of extensive chemical analysis of six Advanced Wastewater Treatment (AWT) plant effluents. Four plants were located in California, and one each in the District of Columbia and Texas. None of the 63 AWT effluent samples contained concentrations of heptachlor in excess of the detection limit (the detection limit was not reported).

Truhlar and Reed (1976) reported on water samples collected from four streams in Pennsylvania and analyzed for chlorinated hydrocarbon pesticides during the period from April 1970 to February 1971. The streams drained four different types of land use areas. Concentrations of heptachlor and heptachlor epoxide were not detected in any of the 25 stream samples.

Schacht (1974) presented the results of a study to determine the levels of pesticides in the surface water of Lake Michigan and its tributaries. During the period 1970 to 1972, a total of 45 water samples were collected. Concentrations of heptachlor epoxide ranging from "non-detected" to 0.017 ug/l were found in the samples. The detection limit for heptachlor epoxide was reported as less than 0.0002 ug/l.

Dappen (1974) reported the results of a study to determine the pesticide content of urban storm runoff in Nebraska. Runoff samples were collected at three stations in a Nebraska city during and after storms. A total of 80 samples were collected at the first station during 16 different storms. Concentrations of heptachlor and heptachlor epoxide in samples from the first station ranged from 0 to 0.059 ug/l and 0 to 0.2 ug/l, respectively. At the second sampling station, 55 samples were collected during 9 different storms. Concentrations of heptachlor and heptachlor epoxide in samples from the second station ranged from 0 to 0.176 ug/l and 0 to 0.194 ug/l, respectively. A total of 14 samples were collected at the third station during 3 storms. Concentrations of heptachlor in samples from the third station ranged from 0 to 0.055 ug/l. No heptachlor epoxide was detected. No detection limits were reported for the study.

8.2.2 Ambient Air

Several studies have been performed by EPA in recent years to determine levels of pesticides in ambient air. Kutz et al. (1976) reported on levels of heptachlor in the ambient air of 16 states between 1970 and 1972. The maximum level measured was 0.0278 ug/m³ in Tennessee; the mean value for all positive samples was 0.001 ug/m³. Heptachlor was detected in 42 percent of the 2,479 samples collected during the monitoring period (no detection limit was reported). Although the frequency of detection increased slightly during the study period (38-44%), the mean of positive samples declined from 0.0014 to 0.0007 ug/m³. Kutz et al. (1976) cautioned that the sampling locations in these studies were selected for potentially high concentrations of pesticides in ambient air.

Kutz et al. (1976) also presented the results of a pilot suburban air monitoring program that was conducted between April and June 1975. During that period, five duplicate samples were collected in suburban areas of Miami, Florida; Jackson, Mississippi; and Fort Collins, Colorado. Heptachlor was detected in all of the samples collected near Miami and Jackson at mean values of 0.0021 and 0.011 ug/m³, respectively. None of the samples collected from Fort Collins, Colorado, contained detectable levels of heptachlor (no detection limit was reported). The maximum value of heptachlor measured in the 30 samples was 0.0221 ug/m³. Heptachlor epoxide was detected in 20 percent of the samples from Jackson, Mississippi, with a maximum reported value of 0.0013 ug/m³. No heptachlor epoxide was detected in samples from Florida or Colorado.

Arthur et al. (1976) collected and analyzed air samples from the Mississippi Delta, one of the highest pesticide usage areas in the United States due to the intensive cotton production. Between 1972 and 1974, samples were collected at weekly intervals; a total of 156 samples was obtained. The maximum heptachlor level reported was 0.008 ug/m³. No other information was reported regarding levels of pesticides monitored during the sampling period.

Kutz et al. (1976) presented the results of a pilot suburban air monitoring program that was conducted between April and June 1975, reporting a

maximum heptachlor epoxide concentration of 0.0013 ug/m³ and that heptachlor epoxide was detected in 20 percent of the samples from only one of the three sites. No detection limit was reported.

Arthur et al. (1976) reported finding a maximum heptachlor epoxide level of 0.0093 ug/m³ among 156 samples collected weekly from the Mississippi Delta between 1972 and 1974.

8.2.3 Soil/Sediments

One soil study and two sediment studies were identified that examined the occurrence of heptachlor and heptachlor epoxide. Carey et al. (1978, 1979) presented data collected during the 1971 and 1972 National Soils Monitoring Program. During the late summer and fall of 1971, composite soil samples were obtained from 1,486 10-acre sites in 37 states. Data were collected from 1,483 sites in the same states in the summer and fall of 1972. During the 1971 sampling program, heptachlor was detected in 73 (or 5%) of the 1,486 samples, in the range of 10 to 1,370 ug/kg. Heptachlor epoxide was detected in 103 (or 7%) of the 1,486 samples, in the range of 10 to 430 ug/kg. During the 1972 collection program, heptachlor was detected in 57 (or 4%) of the 1,483 samples, in the range of 10 to 600 ug/kg. Heptachlor epoxide was detected in 97 (or 7%) of 1,483 samples, in the range of 10 to 720 ug/kg. The minimum detection limits for organochlorines ranged from 2 to 30 ug/kg.

Britton et al. (1983) reported on levels of pesticides in water-sediment mixtures (unfiltered samples) and in bottom material samples collected by the National Stream Quality Accounting Network (NASQAN) in 1976. Throughout the United States, 151 permanent stations, plus stations added as part of local programs, were sampled for pesticides, including heptachlor. Water-sediment mixtures were collected quarterly; bottom materials were collected semi-annually. During 1976, 169 water-sediment samples and 153 bottom material samples were collected. Heptachlor was detected in water-sediment samples at 1 of 13 stations in the Texas-Gulf region and 1 of 5 stations in the Lower Colorado region. The maximum level of heptachlor found at these stations was 0.05 ug/l. Only one of six bottom material samples collected in the Arkansas-White-Red region had a detectable level of heptachlor, at 4.8 ug/kg. Heptachlor

epoxide was detected in one of six water-sediment samples from the California region, at a level of 0.01 ug/l. The detection limits for heptachlor and heptachlor epoxide in the water-sediment and the bottom material samples were not reported.

Schacht (1974) presented the results of a study to assess the levels of pesticides in the sediments of Lake Michigan and its tributaries. During the 1970-1971 collection period, a total of 50 sediment samples were collected from tributaries to Lake Michigan, at stations 40 to 80 yards offshore of sewage treatment plant discharges into Lake Michigan and at open water stations 1 to 3 miles offshore in Lake Michigan. Levels of heptachlor in samples collected in the tributaries ranged from "non-detected" to 0.24 ug/kg, with an average concentration of 0.06 ug/kg. No heptachlor was detected in samples collected at the stations in Lake Michigan. Heptachlor epoxide was identified in samples collected in Lake Michigan, in the range of "non-detected" to 1.35 ug/kg, with the maximum concentration of 1.35 ug/kg found in a sample collected 40 to 80 yards offshore of a sewage treatment plant discharge. In addition, heptachlor epoxide was found in samples collected in the tributaries to Lake Michigan, in the range of 0.02 to 57 ug/kg. The detection limits for heptachlor and heptachlor epoxide in sediments were 0.0025 and less than 0.0025 ug/kg, respectively.

8.2.4 Food

Several estimates of dietary intake of heptachlor and heptachlor epoxide have been reported for recent years. The Food and Drug Administration (FDA) includes heptachlor and heptachlor epoxide among the contaminants analyzed for in its Total Diet Studies (also known as the Market Basket Surveys) to evaluate the daily intake estimates for the adult male, 6-month old infant, and 2-year old toddler (Gartrell et al. 1986a,b).

The total heptachlor intake for the adult male in FY 81/82 was 0.0757 ug/day. The grain and cereal products group contributed 100 percent of the intake. The total heptachlor epoxide intake for the adult male in FY 81/82 was 0.467 ug/day. The meat, fish, and poultry and the dairy products categories accounted for 39.6 percent of the total intake of heptachlor epoxide by the adult male.

The primary contributor to heptachlor epoxide intake by infants and toddlers in FY 81/82 was the whole milk category, accounting for 79.5 and 39.6 percent of intake, respectively. Other dairy and dairy substitutes were also significant contributors to the toddler diet (38.5%). Drinking water did not contribute heptachlor epoxide to the diets of infants or toddlers in FY 81/82.

The FDA provided mean daily intakes of heptachlor and heptachlor epoxide reflecting detections of both contaminants in twelve total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old, daily intake of heptachlor was 0.0001 ug/day; daily intake of heptachlor epoxide was 0.029 ug/day. For the 2-year old toddler, heptachlor intake was 0.0001 and heptachlor epoxide intake was 0.080 ug/day. Heptachlor and heptachlor epoxide intakes for adult males and females are presented in Table 8-1. For the adult male, heptachlor intakes ranged between 0.0001 and 0.0007 ug/day; heptachlor epoxide intakes ranged from 0.132 to 0.184 ug/day. Daily heptachlor intakes for adult females ranged between 0.0001 and 0.0003 ug/day; heptachlor epoxide intake ranged from 0.098 to 0.114 ug/day. The dietary intake of heptachlor is significantly lower than the intake of heptachlor epoxide (FDA 1986), reflecting the conversion of the compound in the environment.

Table 8-3. Summary of FDA Total Diet Study Estimates for Heptachlor and Heptachlor Epoxide Intakes for Adult Males and Females

Sex/Age Group	Intake (ug/day)	
	Heptachlor	Heptachlor Epoxide
14-16 year old female	0.0001	0.112
14-16 year old male	0.0001	0.168
25-30 year old female	0.0002	0.114
25-30 year old male	0.0007	0.184
60-65 year old female	0.0003	0.098
60-65 year old male	0.0002	0.132

Source: FDA 1986

The low-level detection of heptachlor in 42 percent of almost 2,500 air samples taken from 16 states between 1970 and 1972 provides an indication of removal occurring from water and soil by volatilization. Although the locations sampled had been selected for the potential of experiencing high levels of pesticides present in the ambient air and thus the percent of detectable measures was greater than would have resulted from a truly random survey, the maximum concentration measured only 0.0278 ug/m³. Again, due to restrictions imposed, current levels in the ambient air are expected to be lower.

The information currently available on the occurrence of heptachlor and heptachlor epoxide in the environment and the potential for exposure is insufficient to determine the national distribution of intake by any of the three routes, for either compound (Tables 8-2 and 8-3). However, taking into consideration that the data reported for drinking water and air exposure were

Table 8-2. Exposure Estimates for Heptachlor

Source	Reported Exposure Levels	Estimated Adult Intake
Drinking Water	<0.1 ug/m ³	<0.2 ug/day
Diet	--	0.0007 ug/day
Air	?	?

Table 8-3. Exposure Estimates for Heptachlor Epoxide

Source	Reported Exposure Levels	Estimated Adult Intake
Drinking Water	<0.1 ug/m ³	<0.2 ug/day
Diet	--	0.184 ug/day
Air	?	?

derived from studies conducted during the early to mid-1970s (prior to restriction of the use of heptachlor) and that data for food exposure were collected during the early to mid-1980s; therefore, it is likely that current inhalation and drinking water exposure levels will be much less than the reported levels and that current dietary exposure levels will be similar to the reported levels. While exposure to heptachlor is expected to be equally minimal from all three sources, diet is likely to be the greatest source of exposure to heptachlor epoxide.

Because the ranges of potential intake levels from drinking water and air exposure are so wide and varied for both compounds and because the estimated intake levels provided for food are single values and were collected under different usage conditions, it is not possible at this time to generate an accurate estimate of the total exposure to either heptachlor or heptachlor epoxide. Additional data are needed to evaluate current exposure levels and to provide a comparable basis for estimating the total combined intake from each media.

9. LINDANE

9.0 SUMMARY

Lindane is a widely used insecticide. Due to its rapid volatilization from soils and surface waters, levels of lindane in drinking water are expected to be very low for most systems. Monitoring of lindane, while limited, suggests that it will not occur at levels greater than 0.1 ug/l.

9.1 GENERAL CHARACTERISTICS

9.1.1 Physical/Chemical Properties

Lindane gamma-hexachlorocyclohexane, gamma-benzene hexachloride) is the active ingredient of benzene hexachloride (BHC) (NAS 1977). Synonyms and identifiers for lindane include the following (Berg 1986):

Agronexit	Gammex	Lindagranox
Exagamma	Gammexane	Lindalo
Forlin	Inexit	Lindamul
Gallogamma	Isotox	Lindapoudre
Gamaphex	Lacco Hi Lin	Lindaterra
Gammacol	Lacco Lin-O-Mulsion	Lin-O-Sol
Gammalin	Lindafor	Nexit
Gamma BHC	Lindagam	Novigam
Gamma HCH	Lindagrain	Silvanol

Lindane is a crystalline substance at 25°C and has a musty odor (Windholz 1976). It has a molecular weight of 290.85, a molecular formula of $C_6H_6Cl_6$, and a melting point of 112.5°C. The aqueous solubility of lindane at 25°C is 7.8 mg/l (2.7×10^{-5} mol/l) and it has reported vapor pressures at 20°C of 1.6×10^{-4} torr (2.1×10^{-7} atm) (Mabey et al. 1981) and 9.4×10^{-6} torr (Callahan et al. 1979).

The ratio of the highest reported vapor pressure at 20°C to the aqueous solubility at 25°C gives an estimated Henry's constant for lindane at 20-25°C of 7.8×10^{-6} atm·m³/mol. The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an

estimated dimensionless Henry's constant for lindane at 200-250C of 3.2×10^{-4} . Reported K_{OC} values for lindane include 911 (Kenaga and Goring 1978) and 1.08×10^3 (Rao and Davidson 1980).

9.1.2 Use

The USDA (1980a) reports 555 Federal registrations for products containing lindane and 86 state-registered products for which Federal registrations have been requested. The registrations are for the use of lindane-containing products on a large number of fruit and vegetable crops, including pineapples, pecans, and avocados; on lawns, turf, and commercial ornamentals; on commercial and government forests and timberlands; on Christmas trees; as a seed treatment on field crops; as dips and sprays for livestock, pets, and their premises; and as a treatment for controlling parasites that infest humans (USDA 1980a; USEPA 1980e).

In February 1977, EPA issued a notice of a rebuttable presumption against registration and continued registration of pesticide products containing lindane. In 1983, EPA's Office of Pesticide Programs issued Lindane Position Document 4 (USEPA 1983d). In a summary of its regulatory position, EPA (USEPA 1983d) listed restrictions for the use of lindane on commercial ornamentals, avocados, pineapples, pecans, livestock, Christmas trees, structural treatments, forestry, and dog dusts, and washes and in household products including flea collars, shelf paper, and household sprays. Additional household uses were cancelled in 1984 (Kuch 1986).

Lindane is used nationwide as an insecticide. EPA reports 0.8 to 1 million pounds of lindane used in 1986 (Kuch 1986). Major use areas are Hawaii, the Midwest, Federal forest areas, the South, and California.

9.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of lindane is divided into the following subsections: 9.1.3.1 Volatilization; 9.1.3.2 Sorption and Leaching Potential; 9.1.3.3 Abiotic Transformations; 9.1.3.4 Biodegradation and Persistence in Soil and Water; and 9.1.3.5 Summary. The discussion will emphasize the environmental fate of lindane in soil and water.

9.1.3.1 Volatilization

Lyman et al. (1982) indicate that compounds such as lindane ($H = 7.8 \times 10^{-6} \text{ atm}\cdot\text{m}^3/\text{mol}$) with Henry's constants between 10^{-6} and $10^{-5} \text{ atm}\cdot\text{m}^3/\text{mol}$ may undergo significant rates of volatilization from surface waters under favorable conditions (e.g., shallow and/or turbulent waters) but not under unfavorable conditions (deep and/or stagnant waters). Volatilization half-lives estimated for lindane in rivers or streams and in turbulent lakes using equations A-1 and A-3 through A-8 support that conclusion. Estimated volatilization half-lives for lindane in rivers or streams range from 4.4 days in a shallow turbulent river or stream to 1.4 years in a deep low flow river or stream (see Appendix A). Estimated volatilization half-lives for lindane in turbulent lakes range from 7.7 days in a lake 1 m deep to 120 days in a lake 10 m deep.

The estimated volatilization half-lives given above were computed using a reported vapor pressure of 1.6×10^{-4} torr. However, a vapor pressure of 9.4×10^{-6} torr has also been reported for lindane. If the lower reported vapor pressure had been used to estimate volatilization half-lives, the estimated volatilization half-lives would have been long even in shallow turbulent waters (Callahan et al. 1979).

The volatilization rates of lindane from groundwater to the soil column above are projected to be substantially less than those from surface waters to the atmosphere. This is due primarily to the laminar (nonturbulent) nature of ground water flow. Transport from ground water by volatilization may be further reduced by a build-up of lindane in the pore air at the pore air/ground water interface, and an associated decrease in concentration gradient across the interface.

By substituting the mean K_{oc} value for lindane of 1.0×10^3 into equation A-9 along with the compound's highest reported vapor pressure (1.6×10^{-4} torr) and aqueous solubility (7.8 mg/l), SAIC estimates the volatilization half-life for lindane on the soil surface to be 0.78 days. If the lower reported vapor pressure (9.4×10^{-6} torr) is used in the computations, the estimated volatilization half-life for lindane on soil is 13 days. In either

case, volatilization appears to be an important removal process for lindane on the soil surface.

Volatilization rates for lindane beneath the soil surface would be expected to decrease rapidly with depth. Jury et al. (1983) developed a mathematical model for describing transport and loss of soil-applied organic chemicals. Using this model, the authors calculated cumulative volatilization of lindane after 0 days, expressed as a percent of the 1 kg/ha amount initially incorporated. Assuming no water evaporation, the results indicated a maximum of 32.6 percent volatilization (depth of incorporation = 1 cm, organic carbon fraction = 0.0125, boundary layer thickness = 0.5 mm) and a minimum of 1.9 percent volatilization (depth of incorporation = 10 cm, organic carbon fraction 0.0250, boundary layer thickness = 5 mm). The authors concluded that for shallow incorporation of lindane under well-mixed surface conditions, volatilization represents a significant loss pathway. However, the importance of volatilization decreases rapidly with soil depth.

9.1.3.2 Sorption and Leaching Potential

Substituting the mean K_{OC} value of 1.0×10^3 (Section 9.1.1) into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) for lindane ranging from 10 to 80 for sediments or soils, with organic carbon fractions ranging from 0.01 to 0.08, respectively. The estimated $K_{S/W}$ values indicate that at equilibrium, the concentration of lindane in suspended or exposed bottom sediment may be more than 10 times the concentration in the water column. However, since the estimated $K_{S/W}$ values are less than 100, it is unlikely that the ratio of the total mass of lindane adsorbed to suspended and exposed bottom sediment to the total mass of lindane dissolved in the water column will exceed 0.1 in most surface waters. The reason is that in most surface waters most of the time, the ratio of the water mass to the mass of suspended and exposed bottom sediment exceeds 1,000 (USGS 1983). Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are probably not important processes for lindane in most surface waters. That conclusion is supported by studies on the lindane distribution between water and sediment in a flooded quarry and in an oligotrophic lake (Callahan et al. 1979).

Substitution of the mean K_{OC} value of 1.0×10^3 into equation A-13 gives an estimated soil TLC R_f value (Appendix A) of 0.19 for lindane adsorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), lindane would be expected to be at least moderately immobile (Class 2) in, and to be at least moderately resistant to leaching from, surface soil.

9.1.3.3 Abiotic Transformations

There is no information available concerning the hydrolysis of lindane under environmental conditions. However, only negligible losses of lindane over an 8-week period from river water samples with pH values varying between 7 and 8 indicate that hydrolysis probably is not an important removal process for lindane (Eichelberger and Lichtenberg 1971, as cited in Callahan et al. 1979). If it is assumed that the reported neutral first-order hydrolysis rate constant at 20°C for lindane in a 75-percent ethanol mixture with water is the approximate value in water, a hydrolysis half-life of 180 days can be estimated for lindane in water at a pH of 8 (Callahan et al. 1979).

There is no information on the photo-oxidation of lindane in natural waters. However, the compound does not have functional groups that are readily susceptible to oxidation, and attempts to oxidize lindane with strong oxidants such as ozone, chlorine, and potassium permanganate have failed (Leigh 1969, as cited in Callahan et al. 1979).

Although lindane is reported to undergo some limited photolysis in sun light, it is not expected to undergo significant rates of photolysis in the environment (Callahan et al. 1979). The reason is that it does not have any chromophores that absorb light strongly at wavelengths above the approximate solar radiation cutoff at the earth's surface of 290 nm (Callahan et al. 1979; Lyman et al. 1982).

9.1.3.4 Biodegradation and Persistence in Soil and Water

The report that only negligible amounts of lindane were lost over an 8-week period in river water (Eichelberger and Lichtenberg 1971, as cited in Callahan et al. 1979) suggests that biodegradation may not be an important removal process for lindane in at least some natural waters. Estimated mean degradation half-lives of 266 days and 151 days have been reported for lindane in laboratory incubated aerobic and anaerobic soils, respectively (Rao and Davidson 1980). Therefore, lindane has been classified as persistent in soil (e.g., half-life >100 days) by Rao and Davidson (1980).

9.1.3.5 Summary

Based upon the above discussion and the literature review by Callahan et al. (1979), the following tentative conclusions can be made concerning the most likely behavior of lindane in soil and water:

- o Based upon theoretical considerations assuming that lindane has a vapor pressure of 1.6×10^{-4} torr, volatilization may be an important removal process for lindane in some shallow and/or turbulent surface waters, but not in deep and/or stagnant waters or groundwater. If the lower reported vapor pressure of 9.4×10^{-6} torr is assumed, volatilization is unlikely to be an important removal process for lindane in natural waters under any conditions.
- o Based upon theoretical considerations, volatilization is expected to be an important removal process for lindane on the soil surface and beneath the soil surface at shallow depths, but not for lindane in soil at deeper depths.
- o Based upon theoretical considerations and some limited supporting data, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are not expected to be important processes for lindane in surface waters.
- o Based upon theoretical considerations and groundwater monitoring, lindane is predicted to be fairly resistant to leaching from soils.
- o Based upon theoretical considerations and some limited supporting data, lindane is not expected to undergo significant rates of hydrolysis, oxidation, or photolysis in the environment.
- o Based upon its negligible loss from river water over an 8-week period, it appears that biodegradation may not be an important removal process for lindane in at least some natural waters.

- o Lindane has been classified as persistent in soils (e.g., half-life >100 days) based on reported degradative half-lives of 266 and 151 days in aerobic and anaerobic soils, respectively.
- o Due to its apparent resistance to leaching but fairly long persistence in water and soil, lindane is expected to pose a medium- to long-range but low-intensity threat to ground water and surface waters.

9.2 OCCURRENCE IN THE ENVIRONMENT

9.2.1 Drinking Water Sources

This section presents the available data from monitoring studies and surveys to determine the extent of occurrence of lindane in public drinking water supplies and water other than drinking water.

9.2.1.1 Occurrence in Drinking Water

National and regional studies have addressed concentrations of lindane in drinking water. The results of four national studies and seven regional studies are discussed in this section. Where possible, reported levels of lindane in drinking water from groundwater sources and surface water sources have been discussed separately.

Ground Water Sources -- National Studies

The Federal Reporting Data System (FRDS 1984) provides information on public water supplies found to be in violation of current maximum contaminant levels (MCLs). The system is representative of approximately all 47,700 U.S. public ground water supplies. Although the number of ground water systems in the United States that have monitoring requirements for lindane is not provided by the FRDS, the data indicated that there were no violations of the MCL of 4 ug/l for lindane between 1979 and 1983.

A detailed survey of the contaminants in the water supplies of 10 cities was conducted as part of the National Organics Reconnaissance Survey (USEPA 1975b). Two of the systems sampled, located in Florida and Arizona, utilized ground water as their water source. Lindane was not observed above the minimum

quantifiable concentration in samples taken from these water supplies. The minimum quantifiable concentration was not reported.

The 1978 Rural Water Survey (USEPA 1984i) involved the collection of samples from 267 households in rural locations throughout the United States. The majority of the households tested utilized private water supplies; however, samples of water from 71 public drinking water systems of varying sizes using ground water were tested for lindane. Of these, only one public ground water system exceeded the minimum quantification limit of 0.002 ug/l for lindane. The lindane concentration in the water from that system was 0.006 ug/l.

Ground Water Sources -- Regional Studies

Two positive lindane samples out of 107 samples analyzed were found for ground water wells in Idaho (Idaho Department of Health and Welfare 1984). Monitoring for pesticides in drinking water wells is not routinely done; the sampling performed was in response to a particular contamination incident, not for any comprehensive monitoring program. A relatively low mean of 0.0007 ug/l was reported for these two samples, with one sample having a lindane concentration of 0.076 ug/l (no detection limit was reported). It appears that "negative" samples, possibly assigned a detection limit value, were included in the calculation of the mean.

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. Of the 100 ground water supplies sampled utilizing the five aquifers in Florida, none contained lindane in the finished water in excess of the detection limit (detection limit not reported).

Sandhu et al. (1978) summarized results from a rural water supply study in two counties in South Carolina. Waste supplies sampled were outside incorporated municipalities. Samples were taken randomly from wells where there was no pretreatment prior to use. It was not noted whether these supplies were public or private. Also, data were collected of drinking waters from different land use areas in each county (i.e., agricultural, forest, and residential). Data are presented below for agricultural and residential areas. Although the

number of samples and the number of positive samples were not reported, the sample mean and the percent of samples exceeding the detection limit of 0.01 ug/l were reported.

The results of the study by Sandhu and coworkers showed that 58.3 percent of the samples taken in Chesterfield County and 100 percent of the samples taken in Hampton County had concentrations of lindane in excess of the detection limit of 0.01 ug/l (these percentages include forest land use samples). The range, mean, and median values for agricultural samples in Chesterfield County were not: detected - 0.14, 0.037, and 0.005 ug/l, respectively. For residential samples in Chesterfield County, these same values were: not detected - 0.054, 0.009, and 0.016 ug/l, respectively. Concentrations of samples from Hampton County were higher. The range, mean, and median values for the agricultural area samples were 0.010 - 0.27, 0.10, and 0.16 ug/l, respectively. The same values for residential area samples in Hampton County were: 0.14 - 0.32, 0.18, and 0.22 ug/l, respectively.

Achari et al. (1975) reported the results of a study conducted in South Carolina to determine the ambient levels of lindane in ground water. During the study, 27 samples were collected and analyzed. Analysis of the samples showed a range of "non-detected" to 0.021 ug/l lindane, with an average of 0.0012 ug/l. However, the detection limit for lindane and the number of positive samples were not reported.

Benvenue et al. (1972a) conducted a study to determine the extent of organochlorine pesticide contamination of drinking water in Hawaii. A total of 45 samples of finished drinking water was collected from February 1971 to May 1971. Lindane was detected in 2 of the samples, with values of 0.00006 to 0.0004 ug/l (detection limit not given).

Surface Water Sources -- National Studies

Information was obtained from the Federal Reporting Data System (FRDS 1984) on violations of the current MCL of 4 ug/l for lindane. Data were obtained for the years 1979-1983 and include information for all of approximately 11,600 surface water systems in the United States. No violations of

the MCL of 4 ug/l for lindane were reported for samples analyzed during this time period.

In the NORS survey of 10 cities (USEPA 1975b), samples of drinking water were collected from eight systems having surface waters affected by different types of pollution. Samples of water from two of the eight systems analyzed contained lindane. Water from one system in Ohio that utilized raw water contaminated with industrial discharges contained 0.01 ug/l of lindane. The other system located in North Dakota, utilized raw water contaminated with agricultural runoff. Water sampled from this system showed a detectable but nonquantifiable concentration of lindane. The minimum quantifiable concentration for lindane in the NORS study was not reported.

The Rural Water Survey (USEPA 1984i) also presented data on samples of drinking water obtained from surface water sources. Samples were taken from 21 drinking water sources of varying sizes throughout the United States. None of the samples collected from these systems contained concentrations of lindane in excess of the minimum quantification limit of 0.002 ug/l.

Surface Water Sources -- Regional Studies

Irwin and Healy (1978), summarizing data collected during water quality reconnaissance of public water supplies in Florida, reported that none of 16 surface water supplies sampled contained lindane in excess of the detection limit. The detection limit was not reported.

In a study on the effects of forest runoff on the quality of a public surface water supply in Oregon, Elliott (1979) observed an ambient concentration of lindane of 2 ug/l. Sampling data such as the number of samples, number of positive samples, and other information were not provided.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada,

and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including lindane, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

Unspecified Sources -- National Studies

The EPA Water Supply Program (USEPA 1977a) tested 684 drinking water samples from various sources across the country, for pesticide contamination. Levels of lindane of less than 0.001 ug/l were detected in samples from 37 sites, and levels of less than 0.10 ug/l were found at 16 sites. At three additional sites, samples contained lindane levels of 0.160, 0.200, and 0.900 ug/l. The detection limit was not reported. No further information on this study were reported.

Unspecified Sources -- Regional Studies

The Region V survey (USEPA 1975c), conducted in the first three months of 1975, sampled treated water supplies from 83 utilities in USEPA Region V for

organic chemical content. Only one sample exceeded the detection limit for lindane; this sample contained 0.004 ug/l of lindane.

In a report on source identification of pollutants entering a sewage treatment plant, Levins et al. (1979a) tested two drinking water sources in a drainage basin in Georgia. Although the detection limits were not reported, lindane was not detected in either of the two samples.

9.2.1.2 Occurrence in Water Other Than Drinking Water

One national study and six regional studies presented the results of monitored levels of lindane in water other than drinking water.

Ground Water Sources -- Regional Study

Tucker and Burke (1978) presented data on levels of lindane in samples of water collected from 163 wells in nine New Jersey counties. Only two samples contained levels of lindane in excess of the minimum reportable concentration of 0.01 ug/l. The concentrations of the positive samples were 0.01 and 0.9 ug/l, well below the EPA drinking water standard of 4 ug/l.

Surface Water Sources -- National Study

The National Surface Water Monitoring Program (NWMP 1982) presented data on levels of lindane in surface water samples collected throughout the United States between 1975 and 1979. During the 5-year period, 2,480 samples were collected. Although no detection level was reported for lindane, four positive samples were found during testing. The positive samples were collected in California, Texas, and Hawaii, with concentrations ranging from 0.01-0.02 ug/l.

Surface Water Sources -- Regional Studies

Truhlar and Reed (1976) reported the results of analysis of water samples taken from four streams in Pennsylvania, between February 1969 and April 1971, and analyzed for chlorinated hydrocarbon pesticides. The streams drained four

types of land use areas: forests, general farms, orchards, and residential areas. Of the 83 samples collected, 24 were analyzed from the residential area. Three of these samples were from base flow conditions, and the other 21 samples were taken during storm conditions. All three base flow examples contained no lindane (reported as 0.00 ug/l). Concentrations of the 21 storm samples ranged from "trace" to 0.34 ug/l. The mean concentration of the positive samples was 0.08 ug/l, although only one sample exceeded this concentration. The remainder of the samples ranged from "trace" to 0.02 ug/l. No detection limit was reported for the study.

Two surface water samples were tested for lindane in the Beaumont, Texas/Lake Charles, Louisiana area (USEPA 1980e). No lindane was detected in the samples (detection limits not reported).

Dappen (1974) reported the results of a study to determine the pesticide content of urban storm runoff in Nebraska. Runoff samples were collected at three stations in a Nebraska city during and after storms. A total of 80 samples was collected during 16 different storms at the first station. Concentrations of lindane ranged from 0 to 0.848 ug/l. At the second sampling station, 55 samples were collected during 9 different storms. The range of lindane concentrations in the samples was 0 to 1.02 ug/l. A total of 14 samples were collected during 3 storms at the third sampling station. Concentrations of lindane in samples from the third station ranged from "trace" to 0.479 ug/l. The detection limits were not reported.

Benvenue et al. (1972a) conducted a study to determine the extent of organochlorine pesticide contamination of nonpotable waters in Hawaii. A total of 46 samples was collected from several locations on 4 of the islands. Although the number of positive samples for lindane was not given, the concentrations ranged from "not detected" to 0.0034 ug/l (detection limit not reported).

Englande et al. (1978) presented the results of extensive chemical analysis of six Advance Wastewater Treatment plant effluents. Four plants were located in California, and one each in the District of Columbia and Texas. None of the effluents contained detectable levels of lindane. The detection limit was not reported.

9.2.2 Occurrence in Ambient Air

Several studies have been performed by EPA in recent years to determine levels of pesticides in ambient air (Kutz et al. 1976; Carey and Kutz 1983). Kutz et al. (1976) reported on levels of lindane in the ambient air of 16 states between 1970 and 1972. The maximum level measured was 0.0117 ug/m³ in Tennessee; the mean value for all positive samples was 0.0009 ug/m³. Lindane was detected in 68 percent of the 2,479 samples collected during the monitoring period (the detection limit was not reported). Although the mean levels of lindane remained more or less constant during the study, the frequency of detection declined from 84 percent to 49 percent. Kutz et al. (1976) cautioned that the sampling locations in these studies were selected for potentially high concentrations of pesticides in ambient air.

Kutz et al. (1976) also presented the results of a pilot suburban air monitoring program that was conducted between April and June of 1975. During that period, five duplicate samples were collected in suburban areas of Miami, Florida; Jackson, Mississippi; and Fort Collins, Colorado. Lindane was detected in all of the samples collected near Miami and Jackson at mean values of 0.0017 and 0.0023 ug/m³, respectively. Of the samples collected near Fort Collins, 80 percent contained detectable levels of lindane; the mean value was 0.0007 ug/m³. The maximum value measured in the 30 samples was 0.0054 ug/m³. The detection limits for lindane were not reported.

Carey and Kutz (1983) presented a summary of ambient air monitoring data obtained by EPA for selected pesticides at 10 locations in the United States in 1980. The states sampled were South Carolina, Texas, Alabama, California, Mississippi, Montana, and Illinois. Of the 123 samples collected, only 0.8 percent were positive for lindane (the detection limit was not reported). The mean concentration reported was 0.0001 ug/m³; the maximum concentration was 0.0015 ug/m³.

Arthur et al. (1976) collected and analyzed air samples from the Mississippi Delta, one of the highest pesticide usage areas in the United States due to the intensive cotton production. Between 1972 and 1974, samples were collected at weekly intervals; a total of 156 samples was obtained. The

maximum level of lindane reported was 0.0093 ug/m³. No other information was reported regarding levels of lindane monitored during the sampling period.

9.2.3 Soil/Sediments

Several studies were identified that examined the occurrence of lindane in soil and sediments. As expected from lindane's volatility and potential to bind to sediments, lindane levels in soil and sediments are low. These studies (one soil and four sediment studies) are summarized below.

Carey et al. (1978, 1979) presented data obtained during the 1971 and 1972 National Soils Monitoring Program. During late summer and fall of 1971, composite soil samples were obtained from 1,486 10-acre sites in 37 states. Data were collected from 1,483 sites in the same states in the summer and fall of 1972. Although lindane is listed as one of the organochlorine compounds detectable by their methodology, no positive detections for lindane were reported in the soil samples. The minimum detection limits for organochlorines ranged from 2 to 30 ug/kg.

Britton et al. (1983) reported on levels of pesticides in water-sediment mixtures (unfiltered samples) and in bottom material samples collected by the National Stream Quality Accounting Network (NASQAN) in 1976. Throughout the United States, 151 permanent stations, plus stations added as part of local programs, were sampled for pesticides, including lindane. Water-sediment mixtures were collected quarterly; bottom materials were collected semiannually. Lindane was detected in water-sediment samples at 1 of 10 stations in the Arkansas-White-Red region and at 1 of 13 stations in the Texas-Gulf region. The maximum level of lindane found at these stations was 0.01 ug/l. Water-sediment samples from two of six stations in the California region had detectable lindane levels with a maximum concentration of 0.05 ug/l. No samples of bottom material contained detectable levels of lindane. The detection limits for lindane in the water-sediment and the bottom material samples were not reported.

The National Surface Water Monitoring Program (NWMP 1982) presented data on levels of lindane in sediment samples collected between 1975 and 1979. Of 939 sediment samples analyzed, only 2 samples contained detectable concentrations

of lindane, at 0.09 and 0.30 ug/kg. The two positive samples were obtained in Michigan and Pennsylvania, respectively, during the spring and summer of 1977. The detection limits were not reported.

Schacht (1974) presented the results of a study to assess the levels of pesticides in the sediments of Lake Michigan and its tributaries. During the 1970-1971 collection period, a total of 50 sediment samples were collected from tributaries to Lake Michigan, at stations 40 to 80 yards offshore of sewage treatment plant discharges into Lake Michigan, and at open water stations 1 to 3 miles offshore in Lake Michigan. Levels of lindane in samples collected in the tributaries ranged from "non-detected" to 0.15 ug/kg. No lindane was detected in samples collected at the stations in Lake Michigan. The detection limit for lindane in sediments was 0.0025 ug/kg.

USEPA (1980d) reported that 2 ug/kg of lindane were detected in a sediment sample taken from the Calcasieu River (Beaumont, Texas/Lake Charles, Louisiana area) in March 1978.

9.2.4 Food

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the occurrence of various substances, including lindane, in food consumed by adults, toddlers, and infants. According to the results of a recently published survey for FY 81/82, lindane was present in the following food categories: meat, fish, and poultry; sugar and adjuncts; and grain and cereal products (Gartrell et al. 1986a,b). The highest levels of lindane were detected in the sugar and adjuncts category for the adult survey, and in the grain and cereal products category for the infant and toddler survey.

The FDA also estimates dietary intake of contaminants detected in food consumed by adults, infants, and toddlers. In FY 81/82, the total intake of lindane by the adult male was 0.150 ug/day (Gartrell et al. 1986a). The largest sources of lindane were the meat, fish, and poultry group, which contributed 54 percent of total lindane intake, and the sugar and adjuncts group which contributed 51.5 percent. The beverages category, which includes drinking water, did not contribute any lindane to the dietary intake by the adult male.

For the toddler, total intake of lindane in FY 81/82 was 0.0827 ug/day. Total intake was provided by only two sources, the sugar and adjuncts group (89.8%) and the meat, fish, and poultry category (10.2%). The total dietary intake by the infant was 0.0145 ug/day. The grain and cereal products category was the largest source of lindane, accounting for 80 percent of total intake. Drinking water did not contribute any lindane to the dietary intake of infants or toddlers (Gartrell 1986b).

The FDA provided mean daily intakes of lindane reflecting detections of lindane in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of lindane was 0.014 ug/day. For the 2-year old toddler, lindane intake was 0.083 ug/day. Lindane intakes for adult males and females are presented in Table 9-1. For the adult male, lindane intakes ranged between 0.108 and 0.167 ug/day. Daily lindane intakes for adult females ranged between 0.084 and 0.135 ug/day. Intakes were highest for the 14- to 16-year old age group for both sexes.

TABLE 9-1. Summary of FDA Total Diet Study Estimates for Adult Male and Female Lindane Intake

Sex/Age Group	Intake (ug/day)
14-16 year old female	0.135
14-16 year old male	0.167
25-30 year old female	0.097
25-30 year old male	0.157
60-65 year old female	0.084
60-65 year old male	0.108

Source: FDA 1986

9.3 EXPOSURE SUMMARY

Several studies have been conducted which provide useful data on the extent of occurrence of lindane in drinking water, air, and food. Monitoring surveys of public water supplies usually report lindane levels ranging from "non-detected" to 1.0 ug/l. However, actual levels of lindane in public water supplies are generally much lower than this. These low levels are probably the result of lindane's rapid volatilization from soil and surface water and its

persistence in the soil column. Unfortunately, due to its extensive use, low levels of lindane in natural waters may occur in all areas of the United States. In areas of high usage, lindane may also be a common contaminant in air. According to available monitoring data, ambient air levels, in areas selected for potentially high concentrations of pesticides, range from 0.0001 to 0.0117 ug/m³. Recent dietary studies report that the daily intake of lindane for 25-30 year old males ranged from 0.108 to 0.167 ug/day with a mean daily intake of 0.157 ug/day.

Table 9.2. Exposure Estimates for Lindane

Source	Reported Exposure Levels	Estimated Adult Intake
Drinking Water	<1.0 ug/l	<2.0 ug/day
Diet	--	0.2 ug/day*
Air	0 - 0.01 ug/m ³	<0.2 ug/day

*Note: 25-30 year old adult male.

The above table summarizes the exposure levels of lindane in drinking water, food, and air. The drinking water and ambient air exposure levels are presented as the maximum levels expected based on the limited amount of monitoring data available. The dietary exposure is taken from an average of several total diet studies taken from different regions of the United States over several years. (The number is rounded to one significant figure.) The estimated daily intake levels were derived using several exposure assumptions, including an average intake of 2 liters per day of drinking water and 20 cubic meters per day of air.

The currently available information on occurrence of lindane is insufficient to determine the national distribution of intake by any of the three routes. The table indicates that the total non-drinking water intake of lindane is quite low, on the order of a few tenths of a ug/day, and if lindane occurs in drinking water at levels more than a few tenths of a ug/l, it will be the major source of exposure. The number of people who actually receive drinking water exposures greater than a few ug/l is unknown. Restrictions governing the use of lindane, which were imposed by EPA in 1983, may result in a decreased daily intake by all exposure routes in the future.

10. METHOXYCHLOR

10.0 SUMMARY

Methoxychlor is a chlorinated insecticide that is widely used on a number of crops and around livestock. However, because methoxychlor binds tightly to soil, only low levels are found in drinking water. Based on limited monitoring data, levels of methoxychlor in drinking water are expected to be less than 0.1 ug/l. Compliance data submitted to EPA under the interim standard for methoxychlor show no drinking water supply with levels greater than 100 ug/l.

10.1 GENERAL CHARACTERISTICS

10.1.1 Physical/Chemical Properties

Methoxychlor [2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane] is an insecticide used for the control of insects on fruit and shade trees, vegetables, dairy and beef cattle, home gardens, around farm buildings, and in streams (Berg 1986; NAS 1977). Synonyms and identifiers for methoxychlor include Evershield CM and T, Flo Pro McSeed Protectant, and Marlate (Berg 1986).

Technical grade methoxychlor consists of approximately 88 percent of the p,p-isomer with the remaining 12 percent being primarily the o,p-isomer. Both isomers are white crystalline solids at 25°C, have a molecular weight of 345.65, and a molecular formula of $C_{16}H_{15}Cl_3O$ (Windholz 1976; Berg 1986; Kirk-Othmer 1981). The p,p-isomer has a melting point of 98°C and an aqueous solubility of 4.0×10^{-2} mg/l at 24°C. It is very soluble in aromatic, chlorinated, and ketonic solvents (Berg 1986; Windholz 1976). No vapor pressure for methoxychlor could be found in the literature. A K_{OC} value of 8.0×10^4 has been reported for methoxychlor (Kenaga and Goring 1978).

10.1.2 Use

Methoxychlor is registered for use as an insecticide on about 87 crops (including alfalfa; nearly all fruits and vegetables; and corn, wheat, rice, and other grains); beef and dairy cattle; swine, goats, and sheep; and for

agricultural premises, home gardens, and outdoor fogging (NAS 1977). EPA also has registered methoxychlor as a selective chemical for controlling slugs and snails on apricots, cherries, plums, peaches, and ornamental plants (USDA 1980b). Methoxychlor is widely used because of its long residual action against insects and low toxicity to humans (Berg 1986).

In 1976, approximately 1.4 million pounds of methoxychlor (active ingredient) were used on agricultural crops, including alfalfa, tobacco, corn, and hay and forage (Eichers et al. 1978). In 1982, areas producing corn, sorghum, soybeans, wheat, barley, oats, cotton, tobacco, rice, peanuts, and alfalfa in the United States received approximately 650,000 pounds of methoxychlor* (California 1982). Livestock applications accounted for 4,736,000 pounds of methoxychlor (Eichers et al. 1978).

More recent data show that 5 million pounds of methoxychlor were used in 1986 (Kuch 1986). In a survey of 33 states, Gianessi reports that 1.5 million of methoxychlor were used for agricultural purposes (Gianessi 1986).

10.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of methoxychlor is divided into the following subsections: 10.1.3.1 Volatilization; 10.1.3.2 Sorption and Leaching Potential; 10.1.3.3 Abiotic Transformations; 10.1.3.4 Biodegradation; and 10.1.3.5 Summary. The discussion will emphasize the environmental fate of methoxychlor in soil and water.

10.1.3.1 Volatilization

No information was available concerning the vapor pressure of methoxychlor. Therefore, SAIC was unable to estimate volatilization half-lives for methoxychlor in surface waters or on soils. Methoxychlor has been detected in rain and snow, which suggests that volatilization occurs, but no data on volatilization rates are available. Volatilization rates of a number of pesticides on soils have been shown to be proportional to the magnitude of the K_{oc} value (Swan et al. 1979, as

* Personal communication between Herman W. Delvo, Economic Research Service, U.S. Department of Agriculture, and Corinne Macaluso, JRB Associates, June 5, 1984. Data quoted from a computer printout of the 1982 Crop and Livestock Pesticide Usage Survey.

cited in Lyman et al. 1982). Therefore, the relatively large K_{OC} value for methoxychlor of 8.0×10^4 suggests that volatilization may not be an important removal process for methoxychlor on soil.

10.1.3.2 Sorption and Leaching Potential

Substituting the reported K_{OC} value for methoxychlor of 8.0×10^4 into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) for methoxychlor ranging from 800 to 6.0×10^3 for sediments or soils with organic carbon fractions ranging from 0.01 to 0.08, respectively. As discussed in Appendix A, transport by adsorption to suspended sediments and removal by adsorption to bottom sediments may be important processes in some aquatic systems for chemicals with $K_{S/W}$ values as low as 100. Therefore, such processes are likely to be generally important for methoxychlor with estimated $K_{S/W}$ values ranging from 800 to 6.0×10^3 . Freeden et al. (1975, as cited in USEPA 1984g) reported that approximately 50 percent of the methoxychlor in Saskatchewan River water samples were bound to suspended sediment.

Substituting the reported K_{OC} value of 8.0×10^4 into equation A-13 gives an estimated soil TLC R_f value (Appendix A) of <0.1 for methoxychlor adsorbed to a soil with a relatively low organic fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm^3 . Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), methoxychlor would be expected to be immobile and resistant to leaching from soils. The study by Hunt and Sachs (1969, as cited in USEPA 1984g) supports that conclusion. They reported that all of the methoxychlor sprayed once a year over a several year period remained within the top 6 inches of soil and most remained within the top 1 inch of soil.

10.1.3.3 Abiotic Transformations

Wolfe et al. (1977, as cited in USEPA 1984g) list a neutral first-order hydrolysis rate constant and a second-order base catalyzed hydrolysis rate constant at 27°C of $2.2 \times 10^{-8} \text{ M}^{-1}\text{s}^{-1}$ and $3.8 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$, respectively, for methoxychlor. Substitution of those rate constants into equation A-14 (Appendix A) and the resulting pseudo first-order rate constants into equation A-1 gives estimated

hydrolysis half-lives for methoxychlor at 27°C of approximately 1 year over the normal pH range of 6 to 9 for natural waters. Therefore, hydrolysis does not appear to be an important removal process for methoxychlor in natural waters.

Methoxychlor appears to undergo rapid rates of some type of photodecomposition in the presence of naturally occurring organics in some waters but not in others. Wolfe et al. (1977, as cited in USEPA 1984g) reported photodecomposition half-lives in shallow waters for methoxychlor of 2.2, 5.4, and 2.9 hours in three river waters, but detected no decomposition after 2 hours in two other river waters. The photodecomposition is not primarily due to direct photolysis since the photodecomposition half-life for methoxychlor in distilled water is greater than 300 hours compared to 7.3 hours in the presence of added humic acid. Indirect sensitized photolysis and oxidation by singlet oxygen have also been ruled out as the primary mechanism of photodecomposition (USEPA 1984g). Zepp et al. (1976, as cited in USEPA 1984g) suggested that the photodecomposition may involve oxidation by free radicals generated by the photolysis of naturally occurring organics. Even though photodecomposition rates decrease rapidly with depth, it has been suggested that photodecomposition is an important removal process for methoxychlor in natural surface waters since low solubility compounds such as methoxychlor tend to concentrate in organic surface films (USEPA 1984g).

10.1.3.5 Biodegradation and Persistence in Soil and Water

Brockway et al. (1979, as cited in USEPA 1984g) reported an approximately 80 percent decomposition of methoxychlor in a model ecosystem over a 17-week period. Luczak (1969, as cited in USEPA 1984g) reported a greater than 90 percent decomposition of methoxychlor in a polluted surface water over a 28-week period. Biodegradation may have been responsible for at least some of the decomposition, but it is not known whether it was the primary mechanism of removal (USEPA 1984g). As discussed above, photodecomposition may be an important removal process for methoxychlor in surface waters.

Fogel et al. (1982, as cited in USEPA 1984g) reported a "significant" degradation of methoxychlor initially present at 1,000 ppm in a soil under anaerobic conditions after a 100-day incubation, but not under aerobic or sterile conditions. This indicates that biodegradation is primarily responsible for

degradation under anaerobic conditions and that significant rates of biodegradation did not occur under the aerobic conditions. Similar results were reported by Castro and Yoshida (1971, as cited in Callahan et al. 1979). Castro and Yoshida reported that 27 ppm methoxychlor was completely degraded in three out of four flooded (anaerobic) soils after 90 days incubation, but that concentrations of methoxychlor between 11 and 27 ppm remained after 90 days incubation in unflooded (aerobic) soils. They estimated the times required for 50 percent removal of the methoxychlor in the flooded soils to range from 10 days for flooded (anaerobic) soils with high organic content to 45 days for flooded (anaerobic) soils with low organic content. The estimated times required for 50 percent disappearance in upland unflooded (aerobic) soils were all >90 days. Based on the above results, methoxychlor would be classified as non-persistent (half-life <20 days) to moderately persistent (half-life between 20 and 100 days) in flooded anaerobic soil but persistent (half-life greater than 100 days) in aerobic soils (Rao and Davidson 1980).

10.1.3.5 Summary

Based on the above discussion and the literature review by USEPA (1985e), the following conclusions can be made concerning the most likely behavior of methoxychlor in soils and water:

- ° No information could be found or estimates made concerning the volatilization rates of methoxychlor from water. Based on its relatively large reported K_{OC} value (8.0×10^4), volatilization rates from the soil surface may be low.
- ° Based on both theoretical considerations and limited experimental results, transport by adsorption to sediments and removal by adsorption to bottom sediments may be important processes for methoxychlor in many aquatic systems.
- ° Based on both theoretical considerations and limited experimental results, methoxychlor appears to be resistant to leaching from soils.
- ° Based on experimental results, hydrolysis does not appear to be an important removal process for methoxychlor in water. Methoxychlor is susceptible to rapid rates of some type of photodecomposition in some natural waters but not in others.
- ° Biodegradation appears to be the primary removal process for methoxychlor in soils. Removal rates are much greater in anaerobic soils than in aerobic soils. In one study, the times required to remove 50 percent of

1,000 ppm in flooded anaerobic soils ranged from 10 days in soils with high organic content to 45 days for soils with low organic content. The times required to remove 50 percent of 1,000 ppm methoxychlor in aerobic soils were all well above 90 days.

- ° Due to its apparent resistance to leaching, significant contaminations of ground water supplies by methoxychlor are unlikely.

10.2 OCCURRENCE IN THE ENVIRONMENT

10.2.1 Water

The following section presents data available from monitoring studies and surveys to determine the extent of occurrence of methoxychlor in public drinking water supplies and water other than drinking water.

10.2.1.1 Occurrence in Drinking Water

Studies at both the national and regional levels provided monitoring data on the occurrence of methoxychlor in public drinking water supplies. Where possible, reported levels of methoxychlor in drinking water obtained from ground water sources and surface water sources have been discussed separately.

Ground Water Sources -- National Studies

The Federal Reporting Data System (FRDS 1984) provides information on public water supplies found to be in violation of current maximum contaminant level (MCLs). No violations of the current MCL of 100 ug/l were reported for methoxychlor between 1979 and 1983. The National Interim Primary Drinking Water Regulations require all states and primary agencies to report violations of the interim drinking water standards. The reported violations are recorded in the FRDS. EPA believes that the vast majority of supplies have complied with the Interim reporting requirements; therefore, it is unlikely that any drinking water supplies currently exceed 100 ug/l.

The 1978 Rural Water Survey (RWS) (USEPA 1984i) involved the collection of samples from 267 households in rural locations throughout the United States. There were a total of 71 public groundwater supplies of varying sizes providing

drinking water to households sampled in the RWS, although the majority of households sampled used private water supplies. Water from only one public ground water system exceeded the minimum quantification limit of 0.02 ug/l for methoxychlor. The concentration of methoxychlor in the water from that system was 0.09 ug/l.

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) was conducted from June 1977 to March 1981. Finished drinking water samples, collected from 12 ground water systems, were analyzed for methoxychlor. None of the finished drinking water samples contained methoxychlor in excess of the quantification limit of 0.1 ug/l.

Ground Water Sources -- Regional Studies

Irwin and Healy (1978) analyzed data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. None of the finished drinking water samples taken from 100 water supplies using the 5 major aquifers in Florida contained methoxychlor in excess of the detection limit. No detection limit for methoxychlor was reported.

Tucker and Burke (1978) presented data on levels of methoxychlor in samples of water collected from drinking water wells located near industrial zones and landfills in nine counties in New Jersey. None of the samples contained methoxychlor in excess of the minimum reportable concentrations of 0.08 ug/l.

In another study by the Florida Department of Environmental Resources and the U.S. Geological Survey (Holden 1986), drinking water supplies that tap the Floridian aquifer were sampled. The population served by this aquifer exceeds 3 million people. Of the 96 sites sampled, less than eight samples were positive for methoxychlor. No other information was reported.

Twelve towns in Connecticut were sampled by the Connecticut Agricultural Experiment Station in 1984-1985 (Waggoner 1985). Drinking water wells sampled served, collectively, a population of over 573,000. Methoxychlor was not detected at any of 42 locations sampled (total number of samples was not reported). The detection limit was 3.3 ug/l. Similarly, no methoxychlor was found in 88 samples

taken from drinking water wells on Long Island, New York, during 1984 (Holden 1986). The limit of detection was not reported.

Sandhu et al. (1978) summarized results from a rural water supply study in two counties in South Carolina. Water supplies sampled were outside incorporated municipalities. Samples were taken randomly from wells where there was no pretreatment prior to use. It was not noted whether these supplies were public or private. Also, data were collected of drinking waters from different land use areas in each county (i.e., agricultural, forest, and residential). Data are presented below for agricultural and residential areas. Although the number of samples and the number of positive samples were not reported, information on the sample mean and the percent of samples exceeding the detection limit of 0.01 ug/l is available. The results showed that 46 percent of the samples taken in Chesterfield County and 64 percent of the samples taken in Hampton County had concentrations of methoxychlor in excess of the detection limit of 0.01 ug/l (These percentages include forest land use samples). The range, mean, and median values for agricultural samples in Chesterfield County were: not detected - 0.032, 0.003, and <0.01 ug/l (not detected), respectively. For residential samples in Chesterfield County, these same values were: not detected - 0.15, 0.049, and <0.01 ug/l (not detected), respectively. Concentrations of methoxychlor in samples from Hampton County were generally lower. The range, mean and median values for the agricultural area samples were: not detected - 0.027, 0.01, and 0.018 ug/l, respectively. The same values for residential area samples in Hampton County were: not detected - 0.069, 0.032, and 0.005 ug/l, respectively.

Surface Water Sources -- National Studies

Information was collected from the Federal Reporting Data System (FRDS) 1984) on violations of the current methoxychlor MCL of 100 ug/l in all surface water systems in the United States. None of the systems sampled during 1979 to 1983 were found to contain methoxychlor in excess of the current MCL.

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) also presented data on levels of methoxychlor in drinking water from surface water sources. Finished drinking water samples, collected from

104 surface water systems throughout the United States, were analyzed for methoxychlor. None of the finished drinking water samples collected from the 104 surface water systems contained methoxychlor in excess of the quantification limit of 0.1 ug/l.

The 1978 Rural Water Survey (USEPA 1984i) also presented data on levels of methoxychlor in drinking water obtained from surface water sources. Finished drinking water samples were collected from 22 public drinking water systems of various sizes. None of the samples from the 22 systems contained methoxychlor in excess of the minimum quantification limit of 0.02 ug/l.

Surface Water Sources -- Regional Studies

Irwin and Healy (1978) reported on levels of methoxychlor in finished drinking water samples collected from 16 public water supply systems in Florida that use surface water as their source. In this study, none of the samples from the 16 systems contained methoxychlor in excess of the detection limit. The detection limit for methoxychlor was not reported.

Finished drinking water samples collected in 1970 from both the East and West Jefferson Water Works, Mississippi, also showed that methoxychlor was not present (Brodtnann 1976, as cited in USEPA 1984g). The detection limit was less than 0.1 ug/l (the number of total samples was not reported).

In a study on the effects of forest runoff on the quality of a public water supply of Oregon, Elliott (1979) observed an ambient concentration of methoxychlor in 50 ug/l.

The National Academy of Sciences (NAS 1977) reviewed information on a variety of organic chemicals and their presence in public water supplies. No methoxychlor was detected in any samples collected during a New Orleans drinking water survey (NAS 1977). The minimum quantification limit and the number of samples taken were not given in this report.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data

from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean and range), number of samples, and detection limit are presented.

For most of the volatile organics, including methoxychlor, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

10.2.1.2 Occurrence in Water Other Than Drinking Water

One national study and several regional studies addressed levels of methoxychlor in surface water other than drinking water; two sources addressed methoxychlor in groundwater.

Ground Water Sources

Ground water wells in three California counties were sampled by Ramlit Associates, Inc. (1983). The only information reported was a maximum value of 100 ug/l of methoxychlor for 11 positive samples. Other ground water sources

in California and New Jersey were sampled for methoxychlor, where it was detected, although no specific data were reported (Greenberg et al. 1982 and Maddy et al. 1982, as cited in USEPA 1984g).

Surface Water Sources

The National Surface Water Monitoring Program (NWMP 1982) presented data on concentrations of methoxychlor in surface water samples collected throughout the United States between 1975 and 1979. During the 5-year period, 2,480 samples were collected and analyzed. None of the samples contained methoxychlor in excess of the minimum quantification limit, although the limit was not given in the report.

The National Pesticide Monitoring Network examined results of river samples between 1975 and 1980 (Gilliom et al. 1985). Methoxychlor was not detected in 2,761 samples at 172 locations nationwide (detection limit = 0.1 ug/l).

Englande et al. (1978) presented the results of extensive chemical analyses of six Advanced Wastewater Treatment (AWT) plant effluents. Samples of effluent were collected from four plants located in California, and one each in the District of Columbia and Texas. None of the 63 AWT effluent samples contained methoxychlor in excess of the detection limit (no detection limit was reported).

Schacht (1974) presented the results of a study to determine the levels of pesticides in the surface water of Lake Michigan and its tributaries. From 1970 to 1972, a total of 45 water samples were collected from Lake Michigan and its tributaries. Levels of methoxychlor ranging from "not detectable" to 0.106 ug/l were detected in the samples. The detection limit for methoxychlor in water was reported as 0.001 ug/l.

Bradshaw et al. (1972) conducted a study to determine the seasonal variations in pesticide residues in tributary waters to a small lake in Utah. Water samples were collected from 16 stations biweekly from March 1 through July 1, 1970 and weekly or semiweekly through February 1971. Elevated levels of methoxychlor were detected in samples of water entering the lake in late spring (May-June) and late fall (October-November). The maximum level of methoxychlor

was 5.2 ug/l, detected in June. The number of samples collected and the number of positive samples detected were not reported.

Ambient surface water sources from various locations in upstate New York and the San Joaquin Valley, California, were sampled during 1982-1983 and 1978, respectively (Estabrooks, no date; Ramlit Associates, Inc. 1983). Only one of a total of 72 samples was positive for methoxychlor at a concentration of 70 ug/l (detection limit was not reported). This was in the San Joaquin Valley, California.

10.2.2 Ambient Air

Although the presence of methoxychlor in air might be inferred from its presence in rainwater and snow (Strachan et al. 1980, as cited in USEPA 1984g), no data directly addressing levels of methoxychlor in ambient air were obtained.

10.2.3 Soils/Sediments

From reviewing available soil and sediment study results, it appears that methoxychlor is more prevalent in aquatic sediments than in soils.

Seven studies were identified that addressed methoxychlor in soils of the United States (USEPA 1984g). Only one of these studies indicated levels above the detection limit. This study involved collection of soils from croplands in 43 states in 1969; one sample out of 1,729 soils showed a methoxychlor level (0.28 ppm) above the detection limit (0.01 ppm) (Wiersma et al. 1972 as cited in USEPA 1984g). The remaining six studies were conducted between 1968 and 1979 in as many as 35 states, in cropland and urban areas. Methoxychlor was not detected in these studies above the detection limits (USEPA 1984g). The number of samples for each study was not reported.

Four studies that address levels of methoxychlor in aquatic sediments were identified. First, the National Surface Water Monitoring Program (NWMP) presented data on levels of the insecticide in 939 sediment samples collected from 1975 to 1979 (NWMP 1982). The study results indicated that none of the samples analyzed contained methoxychlor in excess of the detection limit. The detection limit was not reported.

A second study (Britton et al. 1983), conducted in 1976 reported levels of pesticides in water-sediment mixtures and in bottom material samples collected at National Stream Quality Accounting Network (NASQAN) stations. Throughout the United States, 151 permanent stations, plus additional stations identified as part of local programs, were sampled for pesticides, including methoxychlor. No methoxychlor was detected in any of the 169 water-sediment mixture samples or in the 153 sediment samples analyzed. The detection limits for methoxychlor in the water sediment and the bottom material samples were not reported.

Schacht (1974) presented the results of a study to determine the levels of pesticides in the sediments of Lake Michigan and its tributaries. During the 1970-1971 study period, a total of 50 sediment samples were collected from tributaries to Lake Michigan, at stations 40-80 yards offshore of sewage treatment plant discharges into Lake Michigan, and in open water stations 1 to 3 miles offshore in Lake Michigan. Levels of methoxychlor were detected in Lake Michigan sediment samples in the range of 0.13 to 6.6 ug/kg, with an average concentration of 1.24 ug/kg. Levels of methoxychlor ranging from 0.19 to 175 ug/kg, with an average concentration of 21.1 ug/kg, were detected in samples collected in the tributaries to Lake Michigan. The detection limit for methoxychlor in the study was 0.01 ug/kg.

The fourth and last study identified (Warry and Chan 1981, as cited in TXNT 1986) involved the collection of sediment samples from the Niagara River. Samples were collected and analyzed approximately every 2 weeks during the 1979-1980 study period. Methoxychlor residues were present in the samples, although the number of samples and the levels of methoxychlor present were not indicated.

10.2.4 Food

The Food and Drug Administration conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the occurrence of various substances, including methoxychlor, in food consumed by adults, toddlers, and infants. According to the results of a recently published survey for FY 81/82, methoxychlor was detected in legume vegetables, dairy products including whole milk, and grain and cereal products. Dairy products had the highest concentration of methoxychlor in the adult, infant, and toddler diets (0.0002, 0.0011, and 0.0003 ppm, respectively) (Gartrell et al. 1986a,b).

The dairy products category was the largest source of methoxychlor for the adult male, accounting for 55.4 percent of total intake. The legume vegetables category was also a significant contributor, accounting for 32.6 percent of total daily methoxychlor intake. The beverage category, which includes drinking water, did not contribute any dietary intake of methoxychlor by the adult male (Gartrell 1986a).

Only two sources, whole milk and other dairy products and dairy substitutes, contributed to methoxychlor intake for the 6-month old infant. Again, whole milk, other dairy products, and dairy substitutes plus grain and cereal products were the sources of methoxychlor in the toddler diet. Grain and cereal products accounted for the single largest source (about 46%) of total daily intake (Gartrell et al. 1986b).

The FDA provided mean daily intakes of methoxychlor reflecting observed levels of methoxychlor in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of methoxychlor was 0.016 ug/day. For the 2-year old toddler, methoxychlor intake was 0.076 ug/day. Methoxychlor intakes for adult males and females are presented in Table 10-1. For the adult male, methoxychlor intakes ranged between 0.099 and 0.110 ug/day. Daily methoxychlor intakes for adult females ranged between 0.075 and 0.085 ug/day. Intakes were highest for the 14- to 16-year old age group for both sexes.

Table 10-1. Summary of FDA Total Diet Study Estimates for Methoxychlor Intakes for Adult Males and Females.

Sex/Age Group	Intake (ug/day)
14-16 year old female	0.081
14-16 year old male	0.110
25-30 year old female	0.075
25-30 year old male	0.099
60-65 year old female	0.085
60-65 year old male	0.101

Source: FDA 1986

10.3 EXPOSURE SUMMARY

Limited data are available on the extent of methoxychlor in drinking water, food, and air, a few surveys provide useful information on occurrence. The reported concentrations of methoxychlor are listed in the table below by source of exposure. The estimate of drinking water exposure is presented in a range to reflect the uncertainty of the exposure data. This uncertainty arises from the limited amount of monitoring data available. The high value was taken from the highest reported concentration of methoxychlor in drinking water in a national survey. While the actual range of occurrence is unknown, EPA believes that the absence of a single violation of the interim standard of 100 ug/l strongly suggests that all systems are currently below this level. This discussion of estimates of exposure to methoxychlor in adults assumes that an average adult male drinks 2 liters of water per day.

Table 10-2. Exposure Estimates for Methoxychlor

Source	Reported Exposure Levels (low-high)	Estimated Adult Intake
Drinking Water	0-0.09 ug/l	0-0.2 ug/day
Diet	--	0.1 ug/day
Air	No data available	--

Dietary exposures to methoxychlor are expressed as a single number. This number is the average of several FDA market basket surveys taken from different regions of the United States between 1982 and 1985. As such, the number is a reasonable estimate of the average dietary intake in the United States. However, some individuals may receive higher levels of exposure.

The currently available information on occurrence of methoxychlor is insufficient to determine the national distribution of intake by any of the three routes. While the table indicates that drinking water exposure can result in higher intakes than food, this should be taken only as a relative indication of the potential for intake by drinking water. The number of people who actually receive drinking water exposures that are greater than dietary exposures is unknown. EPA has no information on present levels of methoxychlor in ambient and indoor air and, therefore, cannot determine the relative significance of intakes by this route for the population as a whole.

11. PENTACHLOROPHENOL (PCP)

11.0 SUMMARY

Pentachlorophenol (PCP) is widely used as a wood preservative, herbicide, and defoliant. Only limited data are available on occurrence in water and food; no information was found on air levels. Levels of PCP reported to occur in drinking water fall into the range of 0 to 10 ug/l.

11.1 GENERAL CHARACTERISTICS

11.1.1 Physical/Chemical Properties

Pentachlorophenol (PCP) is a preservative, herbicide, preharvest defoliant and desiccant, slimicide, and molluscicide. Synonyms and identifiers for PCP are "penta," Dowicide EC-7, DOW Pentachlorophenol DP-2 Antimicrobial, penchlorol, Pentacon, Penwar, Prilttox, Sinituho, and Weedone (Berg 1986).

Technical grade PCP is a buff colored crystal at 25°C composed of 85 to 90 percent PCP and approximately 10 percent 2,3,4,6-tetrachlorophenol (FDA 1981b; Callahan et al. 1979). PCP is a white crystalline solid at 25°C (Verschuieren 1983). It has a molecular weight of 266.35, a molecular formula of C_6Cl_5OH , and a melting point of 190-191°C (Windholz 1976). The pK_a of the phenolic hydrogen is 4.74 (Callahan et al. 1979).

Reported aqueous solubilities for PCP at 20°C included 14 mg/l (Verschuieren 1983), 18 mg/l (FDA 1981b) and 80 mg/l (Windholz 1976). The range of reported aqueous solubilities for PCP is probably due to the dependence of the aqueous solubility on pH. The aqueous solubility of PCP should increase with increasing pH over the approximate pH range of 2.7 to 6.7 due to an increasing ratio of the more soluble anionic form to the undissociated form. The pH dependence of the aqueous solubility should level off above a pH of approximately 6.7, since greater than 99 percent of the PCP at pHs above 6.7 will be in the anionic form.

The vapor pressure of the solid crystalline PCP at 20°C is 1.1×10^{-4} torr (1.4×10^{-7} atm). If it is assumed that the aqueous solubility of undissociated PCP in aqueous solutions is the 14 mg/l reported by Verschueren (1983), the ratio of the vapor pressure to that aqueous solubility gives an estimated Henry's constant for undissociated PCP at 20°C of 2.6×10^{-6} atm·m³/mol. The ratio of the estimated Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated dimensionless Henry's constant for undissociated PCP at 20°C of 1.1×10^{-4} . Within the pH range of most natural waters (6-9), most of the PCP present will be in the anionic form. The aqueous solubility of the anionic form is much greater than the undissociated form so Henry's constant over the pH range of most natural waters should be much smaller than the 2.6×10^{-6} atm·m³/mol for undissociated PCP.

Mabey et al. (1981) estimated a K_{OC} value for undissociated PCP of 5.3×10^4 which is much larger than the experimental K_{OC} value of 900 listed in Kenaga and Goring (1978). Although the pH at which the experimental K_{OC} value of 900 was determined is not listed, it was probably substantially higher than the pK_a for PCP. Because the anionic form of PCP is adsorbed to a lesser extent than the undissociated form, that would explain the large discrepancy between the two K_{OC} values.

11.1.2 Use

On October 18, 1978, EPA published a notice of rebuttable presumption against registration of pesticide products containing PCP based on the risk criteria of teratogenicity and fetotoxicity. Comments were received on this notice and addressed in Position Document 2/3, which was made available to the public on February 19, 1981. In Position Document 2/3, the agency indicated that the use of PCP also posed the risk of oncogenicity because of the presence of the contaminants, hexachlorodibenzo-p-dioxin and hexachlorobenzene. The agency proposed changes in registrations for PCP. Position Document 4, released in July 1984, outlined their final regulatory position on PCP.

The EPA estimate of the total amount of PCP used in 1986 was 45,000,000 pounds (Kuch 1986). The use of PCP as a wood preservative applied to products

such as railroad ties, lumber, timber, plywood, pilings, posts, crossarms, crossties, and poles accounted for 80 percent (or 40 million pounds) of the estimated 1980 domestic annual production (FDA 1981b).

PCP's use on insulation board and in cooling towers, and as a slimicide in pulp and paper mills, accounted for another 11 percent and 6 percent, respectively, of annual domestic production (FDA 1981b).

The remaining uses of PCP include its applications as a preservative to such diverse products as burlap, leather, paints, and petroleum; its use as a termiticide for structural pest control; its use as an herbicide around railroad tracks, ballast railyards, farms and industrial areas, parking lots, fence rows, driveways, highways, and walkways; its use as a mossicide on lawns in western Oregon and Washington; its use as a preharvest defoliant on alfalfa; and its uses as a preharvest desiccant on beans (as a seed treatment), clover, lespedeza, and vetch (FDA 1981b; USDA 1980b).

11.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of PCP is divided into the following subsections: 11.1.3.1 Volatilization; 11.1.3.2 Sorption and Leaching Potential; 11.1.3.3 Abiotic Transformations; 11.1.3.4 Biodegradation; and 11.1.3.5 Summary. The discussion will emphasize the environmental fate of PCP in soil and water.

11.1.3.1 Volatilization

The dimensionless Henry's constant for undissociated PCP cannot be used to estimate volatilization half-lives of PCP in natural waters. The reason is that within the pH range of 6 to 9 normally encountered in natural waters, most of the PCP will be in the anionic form which is predicted to have a much lower Henry's constant than undissociated PCP. Therefore, estimated volatilization half-lives for undissociated PCP should be much lower than for the primarily dissociated, anionic PCP in natural waters.

Volatilization half-lives for undissociated PCP in streams on rivers were estimated by SAIC using equations A-1 and A-3 through A-6. The estimated volatilization half-lives for undissociated PCP in streams or rivers range from 13 days for a turbulent stream or river 1 m deep to 3.6 years in a stagnant stream or river 10 m deep (see Appendix A). Volatilization half-lives for undissociated PCP in turbulent lakes were estimated by SAIC using equations A-1, A-7, and A-8. The estimated volatilization half-lives for PCP in turbulent lakes range from 34 days in a lake 1 m deep to 340 days in a lake 10 m deep.

Since the estimated volatilization half-lives for undissociated PCP in streams or rivers and turbulent lakes are comparable to or longer than many of the half-lives reported for photolysis and biodegradation and since volatilization half-lives for the primarily dissociated PCP in natural waters are expected to be much longer than those for undissociated PCP, volatilization is probably not an important removal process for PCP in natural waters. That conclusion is supported by experimental work. Moss et al. (1983) and Pignatello et al. (1983), both as cited in USEPA (1986), reported negligible losses of PCP from surface waters due to volatilization.

The rate of volatilization of PCP from groundwater to the soil column above is projected to be much lower than the volatilization rate from surface waters to the atmosphere. This is due primarily to the laminar (non-turbulent) nature of ground water flow. Transport from ground water by volatilization may be further reduced by a build-up of chemical in pore air at the pore air/ground water interface and an associated decrease in the concentration across the interface.

11.1.3.2 Sorption and Leaching Potential

It is difficult to predict the sorption and leaching potential of PCP due to a lack of data on the dependence of K_{OC} on pH. Substitution of the estimated K_{OC} value of 5.3×10^4 for undissociated PCP into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) for undissociated PCP ranging from 530 to 4.2×10^3 for sediments or soils with organic fractions ranging from 0.01 to 0.08, respectively. That suggests that a substantial proportion of the total undissociated PCP present in an aquatic

system could be adsorbed to suspended and exposed bottom sediment. However, at pHs exceeding 6, almost all of the PCP present in an aquatic system would be in the anionic form, which does not appear to adsorb to sediments or soils as strongly as undissociated PCP (Callahan et al. 1979). Therefore, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment may be important processes for PCP in acidic waters with a pH less than 5.7 where a substantial proportion of the total PCP present is undissociated. However, the processes are probably much less important for PCP in the great majority of natural waters with a pH between 6 and 9 where most of the total PCP present is in the anionic form.

Substitution of the estimated K_{OC} value for undissociated PCP of 5.3×10^4 into equation A-13 (Appendix A) gives an estimated soil TLC R_f value of <0.1 for undissociated PCP adsorbed to a soil with an organic fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm^3 . Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), undissociated PCP would be classified as immobile and resistant to leaching from soils. However, the decrease in adsorption of PCP by soils with increasing pH suggests that the anionic form of PCP is adsorbed to a lesser extent by soils than the undissociated form and is more susceptible to leaching (Callahan et al. 1979). Therefore, under acidic conditions in which a substantial proportion of the total PCP is undissociated, PCP may be resistant to leaching. However, under neutral or alkaline conditions where most of the total PCP is dissociated, PCP could be susceptible to leaching (Callahan et al. 1979; USEPA 1986).

11.1.3.3 Abiotic Transformations

PCP does not have any groups that are readily susceptible to hydrolysis and it is therefore unlikely to undergo significant rates of hydrolysis in the environment (Lyman et al. 1982; Callahan et al. 1979). Mabey et al. (1981) estimated the second-order rate constants for the oxidation of PCP in aqueous solution by singlet oxygen ($^1O_2$) and peroxy radicals ($RO_2^{\cdot}$) to be $<7 \times 10^3 \text{ m}^{-1}\text{hr}^{-1}$ and $1 \times 10^5 \text{ m}^{-1}\text{hr}^{-1}$. Substituting those rate constants and assumed concentrations for $^1O_2$ and $RO_2^{\cdot}$ in sunlit surface waters of 10^{-12}M and 10^{-9}M , respectively, into equation A-15, and the resulting pseudo first-order rate

constant into equation A-1, gives an estimated half-life for the oxidation of PCP by $^1O_2$ and $RO_2^{\cdot}$ in sunlit surface waters of 290 days. Therefore, the oxidation of PCP by $^1O_2$ and $RO_2^{\cdot}$ in sunlit surface waters does not appear to be an important removal process for PCP in natural waters.

PCP strongly absorbs light with wavelengths above the approximate solar radiation cutoff of 290 nm at the earth's surface and has been reported to undergo rapid rates of direct photolysis in water. Reported photolytic half-lives for PCP in extremely shallow waters at neutral or alkaline pH range from less than 1 hour to 4.6 days (Callahan et al. 1979; USEPA 1986). Therefore, even though photolytic rates decrease rapidly with increasing depth, photolysis appears to be a major removal process for PCP in shallow waters and at the surface of deeper waters.

11.1.3.4 Biodegradation

PCP appears to be susceptible to biodegradation in river water, but only if the microorganisms have become acclimated. Banerjee et al. (1984) and Baker et al. (1980), both as cited in USEPA (1986), reported that no significant rates of PCP biodegradation occurred in previously uncontaminated river water. However, Banerjee et al. (1984) and Pignatello et al. (1983), both as cited in USEPA (1986), reported that significant rates of biodegradation occurred in river waters after a 2 to 3 week lag period and eventually became the dominant removal mechanism for PCP in the waters.

Crosby et al. (1981), as cited in USEPA 1986) reported that degradation half-lives for PCP in soils typically range from 2 to 4 weeks. Therefore, PCP would be classified as nonpersistent in soils (e.g., $t_{1/2} < 20$ days) by Rao and Davidson) (1980). Degradation half-lives are lowest for soils with high organic and/or moisture content, and with temperatures conducive to microbiological activity. Ide et al. (1972), as cited in USEPA 1986) reported that biodegradation was the primary removal process for PCP applied to a rice paddy, and that PCP was almost completely decomposed within several weeks after application.

11.1.3.5 Summary

Based upon the above discussion and the literature reviews by Callahan et al. (1979) and USEPA (1986), the following conclusions can be made concerning the most likely behavior of PCP in soil and water:

- o PCP is unlikely to undergo significant rates of volatilization from surface or groundwater under any conditions normally found in the environment.
- o Transport by adsorption to suspended sediments and removal by adsorption to bottom sediments may be significant processes for PCP in some acidic waters (pH <6) but are unlikely to be important in natural waters within the normal pH range of 6-9.
- o PCP is strongly adsorbed to acidic soils but is generally weakly adsorbed to neutral and alkaline soils. Therefore, PCP may be susceptible to leaching from neutral or alkaline soils, but generally not from acidic soils.
- o Direct photolysis is an important removal process for PCP in shallow waters and at the surface of deeper waters.
- o PCP appears to be susceptible to biodegradation in river waters but only after a 2 to 3 week lag period. After the lag period, biodegradation may become the dominant removal process in some natural waters.
- o Degradation half-lives for PCP in soil typically range from 2 to 4 weeks. Therefore, PCP can be classified as relatively non-persistent in soil. The major removal process for PCP in soils appears to be biodegradation.
- o Due to its immobility in acidic soils and its low persistence in soil, PCP adsorbed to acidic soils is unlikely to contaminate drinking water supplies. However, under neutral or alkaline conditions, the mobility of PCP may be great enough to contaminate some drinking water supplies even though its persistence in soils is relatively low.

11.2 OCCURRENCE IN THE ENVIRONMENT

11.2.1 Water

This section presents the available data from monitoring studies and surveys to determine the extent of occurrence of PCP in public drinking water supplies and water other than drinking water.

11.2.1.1 Occurrence in Drinking Water

Studies at both the national and regional levels have addressed concentrations of PCP in finished drinking water. The results of two national studies and two regional studies are discussed below. Where possible, ground water sources and surface water sources are discussed separately.

Ground Water Sources -- National Study

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) was conducted from June 1977 to March 1981. Finished drinking water samples, collected from 12 ground water systems of varying sizes, were analyzed for PCP. None of the finished drinking water samples contained PCP in excess of the quantification limit of 1.0 ug/l.

Surface Water Sources -- National Study

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) presented data on levels of PCP in drinking water withdrawn from 105 surface water systems located throughout the United States. Of the 105 water supply systems sampled, finished drinking water from only two systems had concentrations of PCP in excess of the quantification limit of 1.0 ug/l. These systems, located in Pennsylvania and Michigan, had concentrations of 12 ug/l and 1.3 ug/l of PCP, respectively.

Surface Water Sources -- Regional Study

Buhler et al. (1973, as cited in Cirelli 1978) identified a PCP concentration of 0.6 ug/l in a sample of finished drinking water collected from a water supply that obtains its raw water from a river in Oregon. The number of samples analyzed, the number of positive samples identified, and the detection limit were not reported.

Unspecified Sources -- National Study

Cirelli (1978) presented unpublished data from the EPA Drinking Water Program. The water supply systems of 108 cities were studied. Low levels of

PCP were detected in samples of drinking water from 86 of the 108 systems sampled. The positive samples had a mean concentration of 0.07 ug/l of PCP; the median concentration was 0.051 ug/l of PCP.

Unspecified Sources - Regional Study

Levins et al. (1979b) sampled drinking water in the Muddy Creek drainage basin in Cincinnati, Ohio. None of the four samples of finished drinking water contained PCP in excess of the detection limit. The detection limit was not reported.

11.2.1.2 Occurrence in Water Other Than Drinking Water

Several reports at both the national and regional levels have discussed occurrences of PCP in water other than drinking water.

Surface Water Sources -- National Study

Although PCP is not routinely monitored by the National Water Monitoring Program (NWMP), PCP was identified in 15 whole water samples collected from five sites in the California Aqueduct between 1974 and 1976. The range of positive values was 0.01 to 16 ug/l PCP. The total number of samples analyzed and the detection limit were not reported (Cirelli 1978).

Surface Water Sources -- Regional Studies

Buhler et al. (1973, as cited in Cirelli 1978) reported on levels of PCP in samples of water collected from the Willamette River in Oregon. Levels of PCP in the river water samples ranged from 0.1 to 0.7 ug/l. The number of samples analyzed, the number of positive samples, and the detection limit were not reported.

Benvenue et al. (1972a) collected a 24-hour composite effluent sample from a sewage treatment plant on the island of Oahu, Hawaii, to determine the extent of organochlorine pesticide contamination. Analysis of the sample showed a concentration of PCP of 2.6 ug/l.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean, range), number of samples, and detection limit are presented.

For most of the volatile organics, including pentachlorophenol, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

Benvenue et al. (1972b) found levels of PCP of 0.01 ug/l in lake water in Hawaii.

Unspecified Sources -- Regional Studies

Buhler et al. (1973, as cited in Cirelli 1978) analyzed levels of PCP in effluent samples from sewage treatment plants in three cities in Oregon. Concentrations of PCP in the positive samples ranged from 1.0 to 4.0 ug/l. The number of samples analyzed, the number of positive samples identified, and the detection limit were not reported.

Levins et al. (1979b) sampled influent to a sewage treatment plant in Ohio to determine the amount of PCP entering the system. One positive sample was identified out of the six samples analyzed. The concentration of this sample was 26 ug/l of PCP. No detection limit was reported.

11.2.2 Ambient Air

The detection of pentachlorophenol in rain water and in snow (Paasivirta et al. 1985; Benvenue et al. 1972b, as cited in Cirelli 1978) offers indirect evidence of its presence in ambient air. Cautreels et al. (1977) reported ambient air concentrations of 0.0057 to 0.0078 ug/m³ in Antwerp, Belgium, and 0.00025 to 0.00093 ug/m³ in Chacaltaya, Bolivia.

11.2.3 Soil/Sediments

Minimal information was available on the occurrence of PCP in soils and sediments. One study involved the collection of sediment samples from nine coastal sites in the vicinity of Portland, Maine. Reported PCP levels ranged between 0.01 and 2.4 ppb (Ray et al. 1983, as cited in TXNT 1986).

11.2.4 Food

11.2.4.1 Dietary Intake

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the occurrence of various substances, including pentachlorophenol, in food consumed by adults, toddlers, and infants. According to the results of a recently published survey for FY 81/82, pentachlorophenol was detected in several categories, including oils and fats; grains and cereal products; meat, fish, and poultry; sugar and adjuncts; and other dairy substitutes. Oils and fats had the highest concentrations of pentachlorophenol in adult, infant, and toddler diets (0.0072, 0.0034, and 0.0073 ppm, respectively) (Gartrell et al. 1986a,b).

Several estimates of dietary intake of pentachlorophenol have been reported in recent years. The largest source of pentachlorophenol for the

adult was the grain and cereal products category, which accounted for 56.4 percent of the intake. The meat, fish, and poultry category also contributed significantly (26.9%). The beverage category, which includes drinking water, did not contribute any pentachlorophenol diet (Gartrell et al. 1986a).

The largest sources of pentachlorophenol intake for the 6-month-old infant were the grain and cereal products and the oils and fats categories, which contributed 47.8 and 36.5 percent, respectively. Meat, fish, and poultry and the grain and cereal products categories were the largest sources of pentachlorophenol intake for the 2-year old toddler (41.9 and 41.4 percent, respectively) (Gartrell et al. 1986b).

The FDA provided mean daily intakes of pentachlorophenol reflecting detections of pentachlorophenol in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of pentachlorophenol was <0.5 ug/day. For the 2-year old toddler, pentachlorophenol intake was <0.7 ug/day.

Pentachlorophenol intakes for adult males and females are presented in Table 11-1. For the adult male, pentachlorophenol intakes ranged between <1.4 and <1.6 ug/day. Daily pentachlorophenol intakes for adult females ranged between <1.0 and <1.1 ug/day. Intakes were highest for the 25- to 30-year old age groups for both sexes.

Table 11-1. Summary of FDA Total Diet Study Estimates for Pentachlorophenol Intakes for Adult Males and Females

Sex/Age Group	Intake (ug/day)
14-16 year old female	<1.0
14-16 year old male	<1.5
25-30 year old female	<1.1
25-30 year old male	<1.6
60-65 year old female	<1.0
60-65 year old male	<1.4

*Intakes are shown as "<" because they are based on findings possibly affected by sporadic reagent contamination, thus leading to possible high results.
Source: FDA 1986.

11.3 EXPOSURE SUMMARY

The data currently available on the occurrence of pentachlorophenol in drinking water and in food are very limited. Data on its presence in air are almost entirely lacking. The continued use of pentachlorophenol as a wood preservative, herbicide, and defoliant, even after EPA's issuance of a notice of rebuttable presumption against the registration of pesticide products containing PCP, provides a continued low-intensity threat of contamination from each route. The low level presence of pentachlorophenol in drinking water is probably due in part to PCP's tendency to become bound to soil and sediment, especially under acidic conditions. Its tendency to bind as well as its susceptibility to biodegrade leads to pentachlorophenol's low persistence and immobility in soils and to the probability that PCP will not be a significant contaminant of drinking water supplies. The potential of PCP contamination of surface water supplies is further reduced by its rapid removal through photolytic processes.

The presence of pentachlorophenol in foods and the mean daily intake of 1.6 ug/day and 1.1 ug/day by 25-30 year old males and females, respectively, as determined by the FDA during surveys conducted between 1982 and 1985, indicates that residues persist. The only data currently available on the presence of pentachlorophenol in air were derived from studies conducted in Antwerp, Belgium and Chacaltaya, Bolivia.

The available data on the occurrence of PCP in air, food, and water is insufficient to characterize the range and distribution of intake by any of these routes. In general, the limited occurrence data suggests that PCP will occur in a small number of surface water systems at concentrations of a few ug/l. PCP tends to bind to many soils, therefore levels in ground water are expected to be lower than surface water; however, the available monitoring data are insufficient to confirm this. Because PCP is used widely as a wood preservative, contamination of drinking water supplies can occur in all areas of the United States. Dietary exposure to PCP is expected to be common. The available data suggest that for the average person the intakes will be less than 1 ug/day. While EPA has no data on the levels of PCP in air in the United States, based on PCP's physical properties, little exposure is expected from this source.

12. 2,4,5-TP

12.0 SUMMARY

2,4,5-TP is an herbicide that was widely used in the 1960's and 1970's. These uses resulted in low-level contamination of a few ground water supplies. Because of the cancellation of 2,4,5-TP's uses in the early 1980's, present and future occurrence levels of the chemical are considered to be unlikely.

12.1 GENERAL CHARACTERISTICS

12.1.1 Physical/Chemical Properties

2,4,5-TP [2-(2,4,5-trichlorophenoxy)propionic acid] is a selective, pre- and post-emergent herbicide that was introduced in 1952; it is available as the amine as well as sodium salts and various esters (NAS 1977). Synonyms and identifiers for 2,4,5-TP include silvex, Aqua-Vex, Ded-Weed, fenoprop, Fruitone T, Kuron, Kurosai, Silvi-Rhap, and Weed-B-Gon (Berg 1986).

2,4,5-TP is a crystalline substance at 25°C (Windholz 1976). It has a molecular weight of 269.53, a molecular formula of $C_9H_7Cl_3O_3$, and a melting point of 181.6°C (Windholz 1976). 2,4,5-TP and technical grade 2,4,5-TP have reported aqueous solubilities at 25°C of 140 mg/l and 180 mg/l, respectively (FDA 1981b; NAS 1977; Verschueren 1983). No vapor pressure for 2,4,5-TP could be found in the literature. A K_{OC} value of 2.6×10^3 has been reported for 2,4,5-TP (Kenaga and Goring 1978). No pK_a value could be found in the literature for 2,4,5-TP.

The aqueous solubilities of most of the salts of 2,4,5-TP are reported to be greater than that of the acid, but no values are given (FDA 1981b). No vapor pressure or aqueous solubilities for the various esters of 2,4,5-TP could be found in the literature. However, by analogy to the structurally similar 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), the various esters of 2,4,5-T are expected to have substantially greater vapor pressures than the acid, but lower aqueous solubilities (SAIC 1981a).

12.1.2 Use

In 1977, domestic production of 2,4,5-TP was estimated to range between 3.7 million and 4.1 million pounds (NAS 1977). Total annual domestic use of the herbicide in 1979 was estimated at 3 million pounds (FDA 1981b; USEPA 1979a). The EPA Administrator suggested a range of use in Position Document 1/2/3 of between 2.8 million and 3.3 million pounds (USEPA 1979a).

In March, 1979, EPA issued an immediate suspension of the sale, use, or distribution of 2,4,5-TP on forest land, rights-of-way, pastureland, for homes and gardens, on commercial and ornamental turf, and on aquatic weeds and ditch banks (USEPA 1979b). The use of 2,4,5-TP on rangeland, rice, sugarcane, orchards, and other noncrop areas was allowed to continue. However, on March 14, 1980, EPA convened hearings to gather additional data on the risks and benefits of using 2,4,5-TP for these purposes. As of 1984, the remaining uses of 2,4,5-TP were cancelled and production of the pesticide was discontinued (Berg 1986).

12.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of 2,4,5-TP is divided into the following subsections: 12.1.3.1 Volatilization; 12.1.3.2 Sorption and Leaching Potential; 12.1.3.3 Abiotic Transformations; 12.1.3.4 Biodegradation and Persistence in Soil and Water; and 12.1.3.5 Summary. The discussion will emphasize the environmental fate of 2,4,5-TP in soil and water.

12.1.3.1 Volatilization

No vapor pressure could be found for 2,4,5-TP in the literature. However, if it is assumed (based on its higher molecular weight and degree of chlorination) that the vapor pressure of 2,4,5-TP is less than the 6×10^{-7} torr reported for 2,4-D, the estimated Henry's constant for 2,4,5-TP (based on the ratio of the vapor pressure to aqueous solubility) would be less than 1.3×10^{-7} atm·m³/mol. Lyman et al. (1982) indicate that compounds such as 2,4,5-TP with a Henry's constant less than 3×10^{-7} atm·m³/mol are less volatile than water. Therefore, the concentration of 2,4,5-TP in water is not expected to decrease due to volatilization. Because the vapor pressures of

the various esters of 2,4,5-TP are expected to be greater and the aqueous solubilities lower than that of the acid, volatilization rates for the various esters of 2,4,5-TP are expected to be substantially greater than those for the acid.

Substitution of the reported K_{OC} value of 2.6×10^3 for 2,4,5-TP into equation A-9 along with the compound's vapor pressure ($<6 \times 10^{-7}$ torr at 25°C) and mean aqueous solubility (160 mg/l at 25°C) gives an estimated volatilization half-life of >30 years for 2,4,5-TP on the soil surface. Volatilization rates for 2,4,5-TP beneath the soil surface are expected to be even slower, decreasing rapidly with increasing depth (Lyman et al. 1982).

12.1.3.2 Sorption and Leaching Potential

2,4,5-TP is a carboxylic acid herbicide. As an ionic chemical, the behavior of 2,4,5-TP in soil is more variable than that of nonionic organic compounds. Nonionics interact predictably with soil organic matter surfaces and are not influenced greatly by the pH of the soil. Carboxylic acids in ionic form, however, may be repelled from negatively charged soil surfaces at high pH. As pH decreases, the amount of both nonionized organic matter and nonionized compound increases. Under these conditions, 2,4,5-TP would behave as a neutral molecule, and thus adsorption would increase. This is reflected in the work of Kenaga and Goring (1978) who reported that at low pH, 2,4,5-TP is strongly adsorbed by hydrated iron and aluminum oxides.

A soil/water partition coefficient (K_{OC}) of 2,600 is reported for 2,4,5-TP (Kenaga and Goring 1978), but the pH is not reported. Based on the soil/water partition coefficient of 2,600, 2,4,5-TP would be expected to have low mobility in soil. However, FDA (1981b) notes that the mobility of 2,4,5-TP varies widely with formulation and soil type. As discussed above, the K_{OC} would be expected to decrease with increasing pH.

12.1.3.3 Abiotic Transformations

By analogy to the esters of 2,4,5-T, the esters of 2,4,5-TP are expected to be susceptible to hydrolysis to 2,4,5-TP. However, it is unlikely that 2,4,5-TP itself will undergo significant rates of hydrolysis in the environment.

It does not have any functional groups that are readily susceptible to hydrolysis (Lyman et al. 1982). No information could be found in the literature concerning the direct photolysis or photo-oxidation of 2,4,5-TP.

12.1.3.4 Biodegradation and Persistence in Soil and Water

Based on similarity of structure to 2,4,5-T, the half-life of 2,4,5-TP in soil is estimated to be 3 to 4 months. The primary transformation product is 2,4,5-trichlorophenol. The half-life of residues of 2,4,5-TP in range grass is reported to be 1 week (FDA 1981b).

12.1.3.5 Summary

Based on the above discussion, the following tentative conclusions can be made concerning the most likely behavior of 2,4,5-TP, its salts, and esters in soil and water:

- o Based on theoretical considerations, volatilization is not expected to be an important removal process for the acid or various salts of 2,4,5-TP. However, by analogy to the esters of 2,4,5-T, volatilization could possibly be a significant removal process for the esters of 2,4,5-TP.
- o Based on a reported K_{OC} value of 2,600 for the acid, the mobility of the acid in soil is predicted to be low. However, the mobility of 2,4,5-TP varies widely with soil type and pH, generally increasing with increasing pH. No information on the mobility of the esters was found in the literature.
- o By analogy to the esters of 2,4,5-T, the esters of 2,4,5-TP are expected to be at least moderately susceptible to hydrolysis to 2,4,5-TP. Based on theoretical considerations, 2,4,5-TP acid is not expected to undergo significant rates of hydrolysis in the environment.
- o By analogy to 2,4,5-T, the half-life of 2,4,5-TP in soil is estimated to be 3-4 months.

12.2 OCCURRENCE IN THE ENVIRONMENT

12.2.1 Water

This section presents the available data from monitoring studies and surveys to determine the extent of occurrence of 2,4,5-TP in public drinking water supplies and water other than drinking water.

12.2.1.1 Occurrence in Drinking Water

Studies at both the national and regional levels have addressed concentrations of 2,4,5-TP in drinking water. The results of four national surveys and six regional studies are discussed in this section. Reported levels of 2,4,5-TP in drinking water from ground water sources and surface water sources have been discussed separately.

Ground Water Sources -- National Studies

The Federal Reporting Data System (FRDS 1984) provides information on public water supplies found to be in violation of current maximum contaminant levels (MCLs). Data are not available on the number of ground water systems in the United States that have monitoring requirements for 2,4,5-TP. However, no violations of the current MCL of 10 ug/l were reported for 2,4,5-TP during the years 1979-1983.

A detailed survey of the contaminants in the water supplies of 10 cities was conducted as part of the National Organics Reconnaissance Survey (NORS) (USEPA 1975b). Two of the systems sampled, located in Florida and Arizona, used ground water as their water source. Water samples taken from these water supplies had concentrations of 2,4,5-TP below the minimum quantifiable concentration, although the minimum quantifiable concentration was not reported in the survey.

The National Screening Program (NSP) for Organics in Drinking Water (Boland 1981) was conducted from June 1977 to March 1981. None of the finished drinking water samples from the 12 systems were found to contain 2,4,5-TP in excess of the quantification limit of 2.0 ug/l.

The 1978 Rural Water Survey (RWS) (USEPA 1984i) involved the collection and analysis for 2,4,5-T of drinking water samples from 267 households located in rural areas throughout the United States. A total of 71 public ground water systems were covered by the survey. None of the samples from the 71 public groundwater systems contained residues of 2,4,5-TP in excess of the minimum quantification limit of 0.1 ug/l.

Ground Water Sources -- Regional Study

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. Finished drinking water samples were collected from 100 water supplies that use the 5 aquifers in Florida. Water samples from 4 of the 100 water supplies contained residues of 2,4,5-TP ranging from 0.04 to 0.30 ug/l.

Another study by the Florida Department of Environmental Resources and the U.S. Geological Survey (Holden 1986) examined drinking water supplies tapping the Floridian aquifer, which serves over 3 million people. The only information available on this 1984 study was that a mean concentration of 0.02 ug/l for 2,4,5-TP was found from 96 locations sampled.

A study known as the Mississippi Pesticide Hazard Assessment Project (MSU 1984) examined drinking water from shallow wells of 10 counties in northwest Mississippi. During 1983-1984, 143 samples were analyzed from the 10 counties and none were found positive for 2,4,5-TP. Some detection limits varied; the highest was 0.015 ug/l, and the lowest was 0.03 ug/l (the number of wells sampled was not reported).

Similarly, 88 samples taken in 1984 from drinking water wells in Long Island, New York showed no positive concentrations found for 2,4,5-TP (Holden 1986). The number of wells and the detection limit were not reported.

Low levels of 2,4,5-TP were found in drinking water wells in Idaho (Idaho Department of Health and Welfare 1984). Monitoring for pesticides in drinking water wells is not routinely conducted; the sampling performed was in response to a particular incident, not for any comprehensive monitoring program.

Eleven of 107 samples were positive with a mean concentration of 0.007 ug/l (range = not detected to 0.62 ug/l). No other information was available.

Surface Water Sources -- National Studies

Information was obtained from the Federal Reporting Data System (FRDS 1984) on violations of the current MCL of 10 ug/l for 2,4,5-TP. The data were obtained for the years 1979-1983, and include information for all surface water systems in the United States. Monitoring results identified one surface water system in North Carolina that violated the MCL of 10 ug/l for 2,4,5-TP for a period of 3 months in 1979.

In the NORS survey of 10 cities (USEPA 1975b), the drinking water systems of 8 cities with surface waters affected by different types of pollution were sampled. Of the eight systems sampled, samples of water from one system whose raw water supply was contaminated with industrial discharges were found to contain 0.02 ug/l 2,4,5-TP. The minimum quantifiable concentration was not reported.

The National Screening Program for Organics in Drinking Water (NSP) (Boland 1981) also contained information on 2,4,5-TP in drinking water from surface water systems. Finished drinking water samples were collected from 105 surface water supplies. None were found to contain residues of 2,4,5-TP in excess of the quantification limit of 2.0 ug/l.

The 1978 Rural Water Survey (RWS) (USEPA 1984i) also presented information on finished drinking water samples obtained from surface water sources. Finished drinking water samples were collected from 21 surface water systems of varying sizes. None of the samples from these systems was found to contain residues of 2,4,5-TP in excess of the minimum quantification limit of 0.1 ug/l.

Surface Water Sources -- Regional Studies

During the 1976 USGS survey of Florida public drinking water supplies, samples of finished drinking water from 4 of the 16 surface water systems

sampled were found to contain 2,4,5-TP at levels ranging from 0.03 to 0.08 ug/l (Irwin and Healy 1978), well below the MCL of 10 ug/l.

In a study on the effects of forest runoff on the quality of a public water supply in Oregon, Elliott (1979) observed an ambient concentration of 2,4,5-TP of 5 ug/l.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean, range), number of samples, and detection limit are presented.

For most of the volatile organics, including 2,4,5-TP, the available data indicated that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

12.2.1.2 Occurrence in Water Other than Drinking Water

Seven reports addressed levels of 2,4,5-TP in surface water other than drinking water; only one report addressed occurrence of 2,4,5-TP in ground water.

Ground water wells were sampled in 1984 from 25 counties in California during the California State Board's Toxic Special Project (Cohen and Bowes 1984). Three positive samples were reported for 2,4,5-TP, with a maximum value of 1.0 ug/l. No other information was reported.

Monitoring data for 2,4,5-TP are available from the National Surface Water Monitoring Program (NWMP 1982) for the years 1975-1978. Of the 1,556 samples taken during the 4-year period, only one sample (0.1%) contained detectable residues of 2,4,5-TP. The positive sample was collected during the summer of 1978 and contained 0.49 ug/l of 2,4,5-TP. No detection limits were reported.

Monitoring data from the National Pesticides Monitoring Network (Gilliom et al. 1985) indicated that between 1975-1980, 1,768 river samples were collected from 167 sites nationwide and analyzed for 2,4,5-TP. Only two samples were found positive, with a detection limit of 0.5 ug/l. No other information was available.

River and stream samples from upstate New York were analyzed for 2,4,5-TP by the New York State Department of Environmental Conservation (Estabrooks no date) during 1982-1983. One sample of 36 was positive at a concentration of 1.6 ug/l (detection limit = 0.12 ug/l).

Truhlar and Reed (1976) reported on water samples taken from four streams in Pennsylvania and analyzed for chlorinated hydrocarbons. The streams drained four different types of land-use areas. Out of the 25 samples collected from April 1970 to February 1971, 2,4,5-TP was detected in only one sample at a level of 0.02 ug/l. The positive sample was taken from the stream that drained the residential area. No detection limit was reported for the study.

The National Research Council of the National Academy of Sciences reported that residues of 2,4,5-TP ranging from 0.01 to 0.21 ug/l were detected in samples of surface water from 15 western states. No further information was supplied regarding the sampling locations or the analytical methods and detection limits (NAS 1977).

Barks (1978) presented the results of a USGS water quality study conducted from April 1973 to July 1974 in the Ozark National Scenic Riverways, Missouri. During the study, 20 surface water samples were collected from three sites on the Current River and one site on Jacks Fork to be tested for pesticide content. Analysis of unfiltered samples found no residues of 2,4,5-TP in excess of the detection limit (the detection limit was not reported).

Englande et al. (1978) presented the results of extensive chemical analysis of four Advanced Wastewater Treatment (AWT) plant effluents. The four plants were located in Lake Tahoe, California; Blue Plains, District of Columbia; and Pomona and Orange County, California. Although none of the 54 AWT effluent samples contained residues of 2,4,5-TP in excess of the drinking water standard of 10 ug/l, mean concentrations of less than 0.016 ug/l and 0.083 ug/l 2,4,5-TP were identified in System 1 and System 2 effluent samples, respectively, of the Pomona AWT. 2,4,5-TP was not detected in the remaining systems. The number of positive samples and the detection limit were not reported.

12.2.2 Ambient Air

No data were obtained on 2,4,5-TP ambient air concentrations. Because of the low vapor pressure of 2,4,5-TP and its esters, air concentrations are expected to be low.

12.2.3 Soil/Sediments

Two studies were identified that examined the occurrence of 2,4,5-TP in sediments. No studies were identified on the 2,4,5-TP occurrence in soil.

The National Surface Water Monitoring Program (NWMP 1982) presented data on levels of 2,4,5-TP in samples of sediment. From 1975 to 1978, 541 sediment

samples were analyzed for residues of 2,4,5-TP; only one sample contained detectable levels of 2,4,5-TP. This positive sample contained 9.11 ug/l of 2,4,5-TP and was collected in the spring of 1978. No detection limits were reported.

Britton et al. (1983) reported on levels of pesticides detected in water-sediment mixtures (unfiltered samples) and in bottom material samples collected by the National Stream Quality Accounting Network (NASQAN) in 1976. Throughout the United States, 151 permanent stations, plus stations added as part of local programs, were sampled for pesticides, including 2,4,5-TP. Water-sediment samples were collected quarterly; bottom material samples were collected semiannually. 2,4,5-TP was detected in water-sediment samples at 1 of 12 stations in the Lower Mississippi region and 2 of 6 stations in the California region. The maximum level of 2,4,5-TP in water-sediment samples at these stations was 2.2 ug/l. No samples of bottom materials contained detectable levels of 2,4,5-TP. The detection limits for 2,4,5-TP in water-sediment and in the bottom material samples were not reported in the study.

12.2.4 Food

Little information was available on the occurrence of 2,4,5-TP in food in the United States; however, the studies that were identified in the literature are summarized here. Levels in food are expected to decrease due to the cancellation of uses of 2,4,5-TP on food crops.

Leidy et al. (1975, as cited in USEPA 1979a) did not detect residues of 2,4,5-TP in apples harvested 29-91 days after 2,4,5-TP was applied to the ground cover under apple trees. However, Cochrane et al. (1976, as cited in USEPA 1979a) reported that the direct application of a 20 mg/l solution of 2,4,5-TP to apple trees (to prevent fruit drop) resulted in residues in unwashed fruit of 97 ug/kg initially, 46 ug/kg at harvest (10 days), and 35 ug/kg after 4 months in storage. Also, after storage, washed fruit contained 2,4,5-TP residues of 15 ug/kg; washed and waxed fruit contained 14 ug/kg.

The available data were insufficient to estimate the typical human dietary intake of 2,4,5-TP in foods today.

12.3 EXPOSURE SUMMARY

The data available on the occurrence of 2,4,5-TP in drinking water and in food are limited and information on its presence in ambient air could not be obtained. However, because of the low vapor pressure of 2,4,5-TP and its esters, air concentrations are expected to be low. 2,4,5-TP, a herbicide used widely during the 1960's and 1970's, has been detected as a low-level contaminant of drinking water supplies and of some foods. The cancellation of many of its major uses in 1979 and the suspension of the remaining uses in 1984 should result in decreasing levels of contamination from all three routes of exposure.

The absence of any widespread violation of the interim standard, along with the available monitoring data, suggests that the extensive use of 2,4,5-TP during the 1970s did not result in contamination of more than a few ug/l. Based on the assumption that adults consume 2 liters of drinking water per day, intake of 2,4,5-TP would not exceed more than 10 ug/day. With the discontinuation of 2,4,5-TP, current levels and exposures of 2,4,5-TP are expected to be less than the levels reported to occur in the 1970s studies.

Table 12-1. Exposure Estimates for 2,4,5-TP

Source	Range of Reported Exposure Levels (low to high)	Estimated Daily Intake
Drinking Water	0.02-5 ug/l*	0.0006-0.1429 ug/kg day
Air	No data available	
Food**	No data available	

*The data provided for drinking water exposure do not present the results of a study conducted in Idaho reporting levels from "not detected" to 520,000 ug/l with a mean of 11 samples of 6,800 ug/l. From the data provided, it appears that the exposure to 2,4,5-TP will be very low and will be derived almost entirely from drinking water. Although data are not available on the occurrence of 2,4,5-TP in air or food, these sources are not expected to be significant routes of exposure. The total combined exposure to 2,4,5-TP is expected to decrease in the future.

13. TOXAPHENE

13.0 SUMMARY

Toxaphene is an insecticide that was widely used on crops and livestock in the 1960's and 1970's. However, due to its ability to volatilize and its limited mobility to move in soil, it has rarely been detected in drinking water. All uses of toxaphene were cancelled in the early 1980s. Current exposures to toxaphene are expected to be minimal and to decrease further in the future.

13.1 GENERAL CHARACTERISTICS

13.1.1 Physical/Chemical Properties

Toxaphene is an insecticide that is produced from the chlorination of camphene. Toxaphene is a mixture of at least 175 compounds, of which the structures of fewer than 10 are known (NAS 1977). Synonyms and identifiers for toxaphene are Attac 4-2, Camphoclor, Camphofene Huileux, Motox, Phenacide, Phenatox, polychlorocamphene, Strobane T-90, Toxakil, and several others (Berg 1986).

Technical grade toxaphene is a yellowish semicrystalline gum with a melting point range of 65°C-95°C (Kirk-Othmer 1981). It has an approximate overall molecular formula of $C_{10}H_{10}Cl_8$ (Windholz 1976) which corresponds to a mean molecular weight of 414. Overall aqueous solubilities at 25°C of 0.50 mg/l and 0.74 mg/l (1.8×10^{-6} mol/l assuming molecular weight of 414) have been reported for toxaphene (Callahan et al. 1979). The overall vapor pressure of toxaphene at 25°C is reported to be between 0.2 torr (2.6×10^{-4} atm) and 0.4 torr.

The ratio of the smallest reported vapor pressure to the largest reported aqueous solubility gives an estimated minimum overall Henry's constant for toxaphene at 25°C of 0.144 atm·m³/mol. The ratio of the estimated minimum Henry's constant to the product of the gas constant times the temperature in degrees Kelvin gives an estimated minimum dimensionless Henry's constant for toxaphene at 25°C of 6.0. Toxaphene has an estimated K_{OC} value of 964 (Mabey et al. 1981).

13.1.2 Use

In 1974, domestic production of the insecticide toxaphene was estimated at 103 million pounds, with approximately 74 million pounds of that amount applied for agricultural uses (USEPA 1977b). By 1976, the estimated production level decreased to 33 million pounds of toxaphene and total domestic usage in 1982 was 16 million pounds (USEPA 1982c). Of those 16 million pounds, 5.9 million pounds were estimated to have been used on field crops (USDA 1983).

In 1982, the Environmental Protection Agency (EPA) published its intent to cancel or restrict registrations of pesticide products containing toxaphene (Federal Register of November 29). All major uses of toxaphene were cancelled, effective within 30 days of the publication of the notice. Some minor uses of toxaphene were permitted to continue until 1986 (USEPA 1982c).

13.1.3 Environmental Transport and Transformation

The discussion of the environmental fate of toxaphene is divided into the following subsections: 13.1.3.1 Volatilization; 13.1.3.2 Sorption and Leaching Potential; 13.1.3.3 Abiotic Transformations; 13.1.3.4 Biodegradation and Persistence in Soil and Water; and 13.1.3.5 Summary. The discussion will emphasize the environmental fate of toxaphene in soil and water.

13.1.3.1 Volatilization

Toxaphene is a complex mixture of chlorinated hydrocarbons with a mean molecular weight of approximately 414, a minimum overall vapor pressure of 0.2 torr, a maximum overall aqueous solubility of 0.74 mg/l, and an estimated overall minimum Henry's constant of $0.144 \text{ atm}\cdot\text{m}^3/\text{mol}$, all at 25°C as discussed in Section 13.1.1. SAIC used those numbers and equations A-1 and A-3 through A-8 to estimate approximate overall volatilization half-lives for the toxaphene mixture in rivers or streams and turbulent lakes. Estimated volatilization half-lives for toxaphene in rivers or streams range from 1.1 hours in a turbulent river or stream 1 m deep to 11 days in a stagnant river or stream 10 m deep (see Appendix A). Estimated volatilization half-lives for toxaphene in turbulent lakes range from 11 hours in a lake 1 m deep to 4.5 days in a lake 10 m deep.

The estimated volatilization half-lives suggest that volatilization would be an important removal process for most or possibly all of the major components of the toxaphene mixture in surface waters under any conditions. However, even though toxaphene is volatile enough to be effectively removed by air stripping (USEPA 1985d), the persistence of low levels of toxaphene residues in aquatic systems over several years (Callahan et al. 1979) suggests that volatilization may not be an important removal process for some of the components of the mixture. Estimated volatilization half-lives are difficult to interpret because toxaphene is a complex mixture of many different polychlorinated compounds. The persistent low levels of toxaphene residues in aquatic systems may be due to the lower volatility components of the toxaphene mixture (Callahan et al. 1979).

Volatilization rates of toxaphene components from ground water to the soil column above are projected to be substantially less than those from surface waters to the atmosphere. This is due primarily to the laminar nonturbulent nature of ground water flow. Transport from ground water by volatilization may be further reduced by a build-up of toxaphene components in the pore air at the pore air/ground water interface, and an associated decrease in the concentration gradients across the interface.

By substituting the estimated overall K_{OC} value of 964 (Mabey et al. 1981) for the toxaphene mixture into equation A-9 along with the mixture's minimum reported vapor pressure (0.2 torr) and maximum reported aqueous solubility (0.74 mg/l), SAIC estimates the overall volatilization half-life for the toxaphene mixture on soil to be less than 1 minute. However, volatilization half-lives for the less volatile components of the mixture would be greater. In addition, volatilization rates of toxaphene components beneath the soil surface should be much slower than at the soil surface.

13.1.3.2 Sorption and Leaching Potential

Substituting the estimated K_{OC} value of 964 into equation A-11 gives estimated sediment or soil/water equilibrium partition coefficients ($K_{S/W}$) for the overall toxaphene mixture ranging from 9.6 to 77 for sediments or soils with organic carbon fractions ranging from 0.01 to 0.08. The estimated $K_{S/W}$

values indicate that at equilibrium the concentration of many of the toxaphene components in suspended or exposed bottom sediment may be 10 or more times greater than the concentration of the same components in the water column. However, since the estimated overall $K_{S/W}$ values are less than 100, it is unlikely that the ratio of the total mass of toxaphene components adsorbed to suspended and bottom sediment to the total mass of toxaphene components dissolved in the water column will exceed 0.1 in most surface waters. The reason is that in most surface waters, most of the time, the ratio of the water mass to the mass of suspended and bottom sediment exceeds 1,000 (USGS 1983). Therefore, transport by adsorption to suspended sediments and removal by adsorption to bottom sediments are probably not important processes for most of the toxaphene components in most surface waters.

Substitution of the estimated K_{OC} value of 964 into equation A-13 gives an estimated overall soil TLC R_f value (Appendix A) of 0.19 for the toxaphene mixture absorbed to a soil with an organic carbon fraction of 0.014, a pore fraction of 0.5, and a soil density of 2.5 g/cm³. Therefore, based on the five mobility classes defined by Helling and Turner (1968) and cited by Hamaker (1975) for a soil with the same properties (Appendix A), the toxaphene mixture overall would be expected to be moderately immobile (Class 2) in, and moderately resistant to leaching from, surface soil. Although some components of the toxaphene mixture may be more susceptible to leaching than the mixture overall, detectable levels of toxaphene have generally not been found in either surface or groundwater supplies (USEPA 1985d).

10.1.3.3 Abiotic Transformations

The toxaphene mixture overall has been estimated to have a hydrolysis half-life exceeding 10 years in water with a pH between 5 and 8 (Callahan et al. 1979). Therefore, hydrolysis does not appear to be an important removal process for toxaphene in natural waters.

No information is available concerning the oxidation of toxaphene in natural waters. Based on the structures of known components of toxaphene, Mabey et al. (1981) estimated a second order rate constant of 3 M⁻¹ hr⁻¹ for the oxidation of the toxaphene mixture overall by sunlight-generated peroxy

radicals. Substitution of that rate constant and an assumed concentration of $1 \times 10^{-9}M$ peroxy radicals in sunlit surface waters into equation A-15 and the resulting pseudo first-order rate constant into equation A-1 gives an estimated half-life of $>10^4$ years for the oxidation of toxaphene by peroxy radicals in surface waters.

The known components of the toxaphene mixture do not have chromophores that absorb light strongly above the approximate solar radiation cutoff at the earth's surface of 290 nm (Lyman et al. 1982). Therefore, the toxaphene mixture is not expected to undergo significant rates of photolysis in the environment. Wolfe et al. (1976), as cited in Callahan et al. (1979) reported that the GC profile of a toxaphene mixture did not change after irradiation by light with wavelengths >290 nm.

10.1.3.4 Biodegradation and Persistence in Soil and Water

At least some of the components of the toxaphene mixture are very persistent in soil, sediments, and water. Callahan et al. (1979) reviewed a number of lake studies in which low levels of toxaphene residues were reported to persist in both sediments and the water column for several years after application. Degradation half-lives of up to 20 years have been reported for the toxaphene mixture overall in aerobic soils and sediments (FDA 1981a). However, toxaphene appears to be susceptible to reduction and much less persistent in anaerobic soils and sediments. Parr and Smith (1976), as cited in Callahan et al. 1979) reported that biodegradation removed 50 percent of toxaphene over a 6-week period in flooded (anaerobic) soil, but that no degradation occurred over the same period in aerobic sediment.

1.3.6 Summary

Based on the above discussion and the review by Callahan et al. (1979), the following tentative conclusions can be made concerning the most likely behavior of toxaphene in soil and water:

- o Based upon theoretical considerations, volatilization is expected to be an important removal process for most or all of the major components of the toxaphene mixture in surface waters and on soil.

- o Based upon theoretical considerations, transport by adsorption to suspended sediment and removal by adsorption to bottom sediment are not expected to be important processes for most or all of the major components of the toxaphene mixture in most surface waters.
- o Based upon theoretical considerations and monitoring data, most or all of the major components of the toxaphene mixture are expected to be at least moderately resistant to leaching from surface soil.
- o Based upon limited data, the major components of toxaphene are not expected to undergo significant rates of hydrolysis nor direct photolysis in the environment. Based upon theoretical considerations, toxaphene is not expected to undergo significant rates of photo-oxidation in the environment.
- o Based upon monitoring data, many of the components of the toxaphene mixture appear to be extremely resistant to biodegradation in aerobic soils and sediments with estimated degradation half-lives of up to 20 years. However, toxaphene appears to be susceptible to both abiotic and biologically mediated reduction in anaerobic soils and sediments.

13.2 OCCURRENCE IN THE ENVIRONMENT

13.2.1 Water

This section presents the available data from monitoring studies and surveys to determine the extent of occurrence of toxaphene in public drinking water supplies and water other than drinking water.

13.2.1.1 Occurrence in Drinking Water

Studies at both the national and regional levels have addressed concentrations of toxaphene in drinking water. The results of three national studies and several regional studies are discussed in this section. Where possible, reported levels of toxaphene in drinking water obtained from ground water sources and surface water sources have been discussed separately.

Ground Water Sources -- National Studies

The Federal Reporting Data System (FRDS 1984) provides information on public water supplies found to be in violation of current Maximum Contaminant Levels (MCLs). Data are not available on the number of ground water systems in the U.S. that have monitoring requirements for toxaphene; however, no violations of the current MCL of 5 ug/l were reported for toxaphene during the years 1979-1983.

The 1978 Rural Water Survey (USEPA 1984i) involved the collection of samples from 267 households (the majority using private water supplies) in rural locations throughout the U.S. and analyses for toxaphene. A total of 71 public drinking water systems of varying sizes using groundwater were covered by the survey. None of the samples from the 71 groundwater systems studied exceeded the minimum quantification limit of 0.17 ug/l for toxaphene.

Ground Water Sources -- Regional Studies

Irwin and Healy (1978) summarized data collected in 1976 during a water quality reconnaissance of public water supplies in Florida. None of the 100 water supplies sampled utilizing the five aquifers in Florida contained toxaphene in excess of the detection limit (the detection limit was not reported).

Tucker and Burke (1978) presented the results of analyses of samples collected from wells in nine New Jersey counties. None of the samples tested contained concentrations of toxaphene in excess of the minimum reportable concentration of 0.06 ug/l for the study.

Surface Water Sources -- National Studies

Data were obtained from the Federal Reporting Data System (FRDS 1984) on violations of the current MCL of 5 ug/l for toxaphene. The data were obtained for the years 1979-1983 and include information for all surface water systems in the United States. The analysis indicated that none of the samples from the surface water systems studied contained toxaphene in excess of the current MCL.

The 1978 Rural Water Survey (USEPA 1984i) also presented data on drinking water samples obtained from surface water systems of varying sizes. None of the samples from the 21 public drinking water systems contained concentrations of toxaphene in excess of the minimum quantification limit of 0.17 ug/l.

Surface Water Sources -- Regional Studies

Irwin and Healy (1978), summarizing data collected during a water quality reconnaissance of public water supplies in Florida, reported that none of the

samples from the 16 surface water supplies studied contained concentrations of toxaphene in excess of the detection limit. The detection limit was not reported.

In a study on the effects of forest runoff on the quality of a public water supply in Oregon, Elliott (1979) observed a concentration of toxaphene of 3 ug/l.

To assemble a database which would reflect the status of Great Lakes drinking water quality, the Canadian Public Health Association gathered data from October 1984 through August 1985 (Canadian Public Health Association 1986). The data collected covered the period from the mid 1970s to early 1985. The study was funded by the Health Protection Branch of Health and Welfare Canada, and the Ontario Ministry of the Environment. The data collected cover the period from the mid-1970's to early 1985. A research team, appointed by the Association, reviewed data on the quality of water at 31 representative Canadian and United States communities and 24 offshore sites to evaluate the human health implications.

For each of the 31 communities, data consisted of: 1) background information on the community; 2) treatment plant schematics and associated treatment process information; and 3) water quality data. Water sample types included raw water (treatment plant intake), distribution water (treated water), and tap water. Water quality data collected included general parameters (e.g., alkalinity, turbidity), microbiological and radiological parameters, inorganic parameters, and organic parameters (including volatiles, base/neutrals, pesticides and PCBs, and phenols and acids). For each parameter, the water type, time period, concentration (mean, range), number of samples, and detection limit are presented.

For most of the volatile organics, including toxaphene, the available data indicate that there were very low levels of these contaminants in the raw, treated, or tap water. Most of the values found were "not detected" or near the detection limit (Canadian Public Health Association 1986).

Unspecified Sources -- National Study

In an EPA survey (USEPA 1977b) of pesticide contamination in commercial drinking water sampled during 1975 and 1976, 27 of 58 samples analyzed were found to be positive for toxaphene. The levels of toxaphene detected were at or below 0.05 ug/l. The detection limit was not reported.

Unspecified Sources -- Regional Study

In a report on source identification of pollutants entering a sewage treatment plant, Levins et al. (1979a) tested two drinking water sources in a drainage basin in Georgia. Although the detection limits were not reported, toxaphene was not detected in either of the samples tested.

13.2.1.2 Occurrence in Water Other than Drinking Water

One national study and several regional studies were performed to monitor levels of toxaphene in water other than drinking water. All of the studies reported on levels of toxaphene in surface water; they are discussed below.

National Study

The National Surface Water Monitoring Program (NWMP 1982) presented data on levels of toxaphene in surface water samples collected throughout the U.S. during the period 1975-1979. During this time, 2,479 samples were collected and analyzed for toxaphene. Although no detection limit was given for toxaphene, 11 positive samples (or 0.4%) were found during testing. The range of positive values was 0.0 to 1.65 ug/l.

Regional Studies

Mattraw (1975, as cited in USEPA 1980b) did not detect toxaphene in any surface water samples collected and analyzed during an organochlorine residue survey in Florida. The number of samples analyzed and the detection limit were not reported.

Toxaphene was detected in 11 (or 55%) of 20 Mississippi Delta lakes sampled by Herring and Cotton (1970, as cited in USEPA 1980b). The maximum reported concentration was 1.92 ug/l (the detection limit was not reported).

13.2.2 Ambient Air

The highest toxaphene concentrations in air are found where toxaphene has been used for agricultural application, particularly in the southern United States and during the growing season. Arthur et al. (1976) collected and analyzed 156 air samples from the Mississippi Delta, site of intensive cotton production, between 1972 and 1974. Average monthly toxaphene concentrations in air were 0.258 ug/m³ in 1972, 0.082 ug/m³ in 1973, and 0.160 ug/m³ in 1974, with a maximum detected concentration of 1.747 ug/m³. No detection limit was reported.

Bidleman et al. (1976, as cited in USEPA 1980b) reported 21 air samples from Rhode Island and Georgia in 1975, and in Arizona and Kansas in 1974, with toxaphene concentrations of 0.00004 to 0.007 ug/m³. The number of positive samples and the detection limit were not reported.

Bidleman (1981, as cited in Reinert et al. 1982) reported an average toxaphene concentration of 0.011 ug/m³ in air samples collected in South Carolina in 1978. The number of samples collected, the number of positive samples identified, and the detection limit were not reported.

The highest reported toxaphene level was 8.7 ug/m³ in a city in Arkansas in 1970, with toxaphene detected in 3.5 percent of the 2,479 samples collected from locations that were selected for their potentially high concentrations of pesticides in ambient air. The mean of the positive samples was 5.2 ug/m³ (Kutz et al. 1976). The detection limit and range were not reported.

13.2.3 Soil/Sediments

Three studies were identified that involved the examination of the occurrence of toxaphene in soil and/or sediments; two were soil studies and one was a sediment study.

Carey et al. (1978, 1979) presented data obtained during the 1971 and 1972 National Soils Monitoring Program. During the late summer and fall of 1971, composite soil samples were obtained from 1,486 10-acre sites in 37 states. Data were collected from 1,483 sites in the same states in the summer and fall of 1972. The minimum detection limits for toxaphene ranged from 50 to 100 ug/kg. During the 1971 sampling period, 92 (or 6.2%) of 1,486 soil samples collected were found to contain residues of toxaphene in the range of 180 to 36,330 ug/kg (Carey et al. 1978). During the 1972 sampling period, 76 (or 5.1%) of 1,483 soil samples analyzed were found to contain residues of toxaphene in the range of 220 to 46,580 ug/kg (Carey et al. 1979).

Patty (1981, 1982, as cited in TXNT 1986) reported that 45 percent toxaphene remained in soils 20 years after (soil) treatment. Between 90 and 95 percent of the toxaphene residues were detected in the 30 cm layer. The range of contamination was not presented.

The National Surface Water Monitoring Program (NWMP 1982) presented data on residues of toxaphene in sediment samples collected between 1975 and 1979. Of the 937 sediment samples analyzed, 11 samples were found to be contaminated with detectable levels of toxaphene. The maximum reported value of toxaphene was 814.49 ug/kg.

13.2.4 Food

13.2.4.1 Dietary Intake

The Food and Drug Administration (FDA) conducts Total Diet Studies (also known as Market Basket Surveys) to evaluate the occurrence of various substances, including toxaphene, in food consumed by adults, toddlers, and infants. According to the results of a recently published survey for FY 81/82, toxaphene was detected in several food categories including meat, fish, and poultry; grain and cereal products; leafy vegetables; root vegetables; garden fruits; and oils and fats. In the adult diet study, the highest concentration of toxaphene was detected in root vegetables (0.0059 ppm) (Gartrell et al. 1986a). Toxaphene was only detected in the oils and fats category of infant and toddler diets. The level of toxaphene in the infant diet was 0.323 ppm, while in the toddler

diet toxaphene was present in oils and fats at a level of 0.0408 ppm (Gartrell et al. 1986b).

The grain and cereal products category accounted for about 62 percent of total dietary intake of toxaphene for the adult male. Meat, fish, and poultry and root vegetables also contributed significantly--12 and 11.3 percent, respectively. (Gartrell et al. 1986a.)

Total daily intake of toxaphene by infants and toddlers was provided by only one source--oils and fats. For infants this totaled 0.658 ug/day and for toddlers intake was 0.493 ug/day (Gartrell et al. 1986b).

The FDA provided mean daily intakes of toxaphene reflecting detections of toxaphene in 12 total diet studies conducted from April 1982 to April 1985 (FDA 1986). For the 6- to 11-month old infant, daily intake of toxaphene was 0.065 ug/day. For the 2-year old toddler, toxaphene intake was 0.310 ug/day. Toxaphene intakes for adult males and females are presented in Table 13-1. For the adult male, toxaphene intakes ranged between 0.576 and 0.603 ug/day. Daily toxaphene intakes for adult females ranged between 0.367 and 0.492 ug/day. Intakes were highest for the 60- to 65-year old age group for both sexes.

Table 13-1. Summary of FDA Total Diet Study Estimates for Toxaphene Intakes for Adult Males and Females

Sex/Age Group	Intake (ug/day)
14-16 year old female	0.367
14-16 year old male	0.584
25-30 year old female	0.369
25-30 year old male	0.576
60-65 year old female	0.492
60-65 year old male	0.603

Source: FDA 1986.

13.3 EXPOSURE SUMMARY

Several studies have been conducted that provide useful data on the extent of occurrence of toxaphene in drinking water, air, and food. According to the monitoring data collected during the late 1970's, most of the reported toxaphene levels in drinking water were below 0.1 ug/l. Current levels in drinking water are unknown because of a lack of data, but are expected to be even lower than in the 1970's due to the restrictions placed on the major uses of the compound in 1982. Also with the cancellation of the remaining minor uses of toxaphene in 1986, coupled with the volatilization and biodegradation of the remaining toxaphene in the environment, future levels in drinking water are not expected to be higher than those levels reported in the past. According to available data from the late 1970's and 1980, ambient air levels in agricultural areas where toxaphene was used were reported to reach as high as 8.7 ug/m³. However, typical levels ranged from less than 0.01 to 1.75 ug/m³. While current data on toxaphene concentrations in ambient air are unavailable, levels today, as well as those in the future, are expected to be negligible. Recent dietary studies report that the daily intake of toxaphene for 25-30 year old males ranged from 0.576 to 0.603 ug/day, with a mean daily intake of 0.576 ug/day. However, future intake levels are expected to decrease. Exposure estimates for toxaphene are presented in Table 13-2.

Table 13-2. Exposure Estimates for Toxaphene

Source	Reported Exposure Levels (low-high)	Estimated Adult Intake
Drinking Water	0 - <0.1 ug/l	0 - <0.2 ug/day
Diet*	--	0.6 ug/day
Air	Negligible	Negligible

* Note: 25-30 year old adult male.

The current available information on occurrence of toxaphene is insufficient to determine the national distribution of intake by any of the three routes. However, EPA believes that intakes from diet will generally be less than 1 ug/day and that air exposure to toxaphene is expected to be negligible. If toxaphene does occur in drinking water at levels of more than a few tenths of a ug/l, it is likely to be the major source of intake. However, for the majority of individuals in the United States diet is the major source.

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APPENDIX A. METHODOLOGIES EMPLOYED FOR CALCULATING
ENVIRONMENTAL FATE PARAMETERS

Half-life Computations

The following equation was used to calculate the half-life for removal of a chemical from a given medium due to a single first order or pseudo first order rate process i:

$$t_{1/2i} = \ln 2 / K_i \quad (\text{A-1})$$

where

$t_{1/2i}$ = half-life in units of time due to removal by process i

K_i = first order or pseudo first order rate constant for the removal of the chemical from the given medium by process i.

The following equation was used to calculate the overall half-life for removal of a chemical from a given medium due to all first order and pseudo first order rate processes for which a rate constant is known or estimated (Mabey et al. 1981):

$$t_{1/2} = \ln 2 / \sum K_i \quad (\text{A-2})$$

Volatilization From Surface Waters

Methods for estimating volatilization half-lives for chemicals in surface water are reviewed by Lyman et al. (1982).

If the concentration of a chemical in the water column is approximately uniform and much greater than the concentration of the chemical in air at the air/water interface, the rate of volatilization will approximately follow first order kinetics so that equation (A-1) can be used to estimate volatilization half-lives (Lyman et al. 1982). The use of equation (A-1) to estimate volatilization half-lives requires the computation of a volatilization rate constant (K_v).

The following equation was used to estimate K_v values for a given chemical (Lyman et al. 1982).

$$K_v = \frac{H' k_g k_l}{(H' k_g + k_l) Z'} \quad (A-3)$$

where

K_v = volatilization rate constant in hr^{-1}
 H' = dimensionless Henry's constant
 k_g = gas phase exchange coefficient in cm/hr
 k_l = liquid phase exchange coefficient in cm/hr
 Z' = mean water depth in cm

The following equations were used to estimate k_g , k_l for wind velocities $< 1.9 \text{ m/s}$ and k_l for wind velocities between 1.9 m/s and 5.0 m/s , respectively.

(Southworth 1979 in Lyman et al. 1982):

$$k_g = 1137.5 V_{\text{wind}} V_{\text{curr}} + V \sqrt{18/M} \quad (A-4)$$

$$k_l = 23.51 V_{\text{curr}}^{0.969} / Z^{0.673} \sqrt{32/M} \quad (A-5)$$

$$k_l = 23.51 V_{\text{curr}}^{0.969} / Z^{0.673} \sqrt{32M} e^{-0.526 (v_{\text{wind}} - 1.9)} \quad (A-6)$$

where

k_g = gas phase exchange coefficient in cm/hr
 k_l = liquid phase exchange coefficient in cm/hr
 V_{wind} = mean near surface wind velocity in m/s
 V_{curr} = mean water current in m/s
 Z = mean water depth in m

Equations (A-4) through (A-6) can be used to compute k_g and k_l values in lakes as well as rivers and streams since lakes also have currents due to

stream inflows, temperature gradients and wind (Reid and Wood 1976). However, lake currents are generally not determined as often as river or stream currents and are therefore frequently not available for incorporation into equations (A-4) through (A-6). Therefore, the following equations derived by Liss and Slater (1974) for the air/sea interface were used in place of equations (A-4) through (A-6) to estimate k_g and k_l for turbulent lakes:

$$k_g = 3000 \sqrt{18/M} \quad (A-7)$$

$$k_l = 20 \sqrt{44/M} \quad (A-8)$$

where

k_g = gas phase exchange coefficient in cm/hr

k_l = liquid phase exchange coefficient in cm/hr

M = molecular weight

However, since the air/sea interface is generally more turbulent than most air/lake interfaces, the values of k_g and k_l computed from equations (A-7) and (A-8) may be too high, and the corresponding estimated volatilization half-lives too low for most lakes (Lyman et al. 1982).

Width and depth averaged river and stream currents can range from <0.1 m/s under stagnant conditions to >10 m/s under storm runoff conditions. However, under non-runoff conditions, most mean river and stream currents fall within the range of 0.2 m/s to 2 m/s (Reid and Wood 1978) which is the range SAIC assumed for computational purposes. Wind speeds can range from <0.1 m/s under stagnant conditions to >30 m/s in storms. However, under non-storm conditions, mean near surface wind velocities typically fall within the range of 0.5 m/s to 5 m/s (Perkins 1974) which is the range SAIC assumed for computational purposes. The mean depths of the Great Lakes range from 17 m for Lake Erie to 148 m for Lake Superior and may exceed 10 m in some sections of a few large rivers (Reid and Wood 1978). However, the mean depths of most rivers, streams, and lakes appear to range from 1 m to 10 m (Reid and Wood 1978) which is the range SAIC assumed for computational purposes.

Volatilization half-lives of chemicals in surface waters decrease with decreasing depth, increasing water current and increasing wind speed. To calculate a theoretical range of typical volatilization half-lives for a given chemical in rivers, streams and turbulent lakes, SAIC did the following:

- o Maximum k_g and k_l values for the volatilization of a given chemical from rivers and streams were estimated by substituting a water depth of 1 m, a current of 2 m/s for river and streams or 0.2 m/s for lakes, a wind speed of 5 m/s and the molecular weight into equations (A-4) and (A-6), respectively
- o Minimum k_g and k_l values were estimated by substituting a water depth of 10 m, a current of 0.2 m/s, a wind speed of 0.5 m/s and the molecular weight into equations (A-4) and (A-5)
- o For comparative purposes, a k_g and k_l value for the volatilization of the chemical from turbulent lakes were also computed by substituting the molecular weight into equations (A-7) and (A-8)
- o Maximum volatilization rate constants (K_v) for the chemical were estimated by substituting a water depth of 1 m, the estimated dimensionless Henry's constant and maximum values of K_g and k_l into equation
- o Minimum volatilization rate constants (K_v) for the chemical were estimated by substituting a water depth of 10 m, the estimated dimensionless Henry's constant and minimum values of K_g and k_l into equation (A-3)
- o Minimum and maximum volatilization half-lives were computed by substituting maximum and minimum volatilization rate constants, respectively into equation (A-1).

Volatilization From Soils

Methods for estimating volatilization half-lives for chemicals in soils are reviewed by Lyman et al. (1982). Due to time restrictions and a lack of the data required to use more sophisticated models, SAIC only used the following equation to estimate the volatilization half-lives of chemicals at the soil surface

$$t_{1/2} = 1.58 \times 10^{-8} \frac{K_{oc} S}{VP} \quad (A-9)$$

where

$t_{1/2}$ = volatilization half-life of the chemical on the soil surface in days

K_{oc} = organic carbon normalized soil/water equilibrium partition coefficient for the chemical and soil of interest

S = aqueous solubility of the chemical in mg/l

VP = vapor pressure of the chemical in torr

Equation (A-9) is only applicable for chemicals applied to and present at the soil surface. In addition, since equation (A-9) was empirically derived from data on chemicals with vapor pressures much less than 1 torr, it was not used to predict the volatilization half-lives at the soil surface of chemicals with vapor pressures exceeding 1 torr.

Sorption and Biomagnification

The equilibrium binding isotherms for the adsorption of organics in aqueous solutions at low concentrations to sediments or soil are frequently linear with near zero intercepts and can be represented by the following equation (Lyman et al. 1982):

$$x/m = K_{s/w} C_{aq} \quad (A-10)$$

where

x/m = μg of chemical adsorbed per g of sediments or soil

$K_{s/w}$ = sediment or soil/water equilibrium partition coefficient

C_{aq} = aqueous equilibrium concentration of the chemical in $\mu\text{g/ml}$ (mg/l)

Although the units of $K_{s/w}$ are ml of aqueous solution lg of sediment or soil, $K_{s/w}$ essentially can be assumed to be unitless since the density of an aqueous solution is generally approximately 1 g/ml.

SAIC used the following equation to predict sediment or soil/water equilibrium partition coefficients for a given chemical and sediments or soils with organic carbon fractions ranging from 0.01 to 0.08 (Lyman et al. 1982):

$$K_{s/w} = K_{oc} f_{oc} \quad (A-11)$$

where

$K_{s/w}$ = sediment or soil/water equilibrium partition coefficient

K_{oc} = organic carbon normalized sediment or soil/water equilibrium partition coefficient

f_{oc} = organic carbon fraction of sediments or soil

K_{oc} values were estimated from the octanol/water partition coefficient and aqueous solubility in Section 1). Equation (A-11) may not be suitable for estimating $K_{s/w}$ values for chemicals adsorbed to sediments or soils with $f_{oc} < 0.01$ or $f_{oc} > 0.08$ (as cited in Lyman et al.).

The sediment or soil/water equilibrium partition coefficient ($K_{s/w}$) can be used to qualitatively predict the behavior of a chemical with respect to adsorption to bottom and suspended sediment, and leaching from soil. However, values of $K_{s/w}$ should be used with caution. As long as the aqueous equilibrium concentration of a chemical is low enough so that its binding isotherm can be represented by equation (A-10), the value of $K_{s/w}$ for the chemical and a given sediment or soil will give the ratio at equilibrium of the μg of chemical adsorbed per g of sediment or soil to the aqueous equilibrium concentration of the chemical in $\mu\text{g}/\text{ml}$ (mg/l). However, at higher aqueous equilibrium concentrations and/or in the presence of high concentrations of other organics which compete with the chemical of interest for binding sites, the equilibrium binding isotherm for the chemical may become non-linear with a decreasing slope and may even decrease to a zero slope if the binding capacity of the sediment or soil is exceeded. In such regions, the value of $K_{s/w}$ will over-estimate the ratio at equilibrium of the chemical concentration in the of sediment or soil to the aqueous equilibrium concentration of the chemical. In addition, if equilibrium has not been obtained, the value of $K_{s/w}$ will be

greater than the actual ratio in a non-equilibrium system in which the concentration of the chemical in solution is still decreasing due to adsorption and will be less than the ratio in a non-equilibrium system in which the concentration of the chemical in solution is still increasing due to desorption (leaching).

It should also be pointed out that at equilibrium, the ratio of the mass of chemical adsorbed to suspended and bottom sediment to the mass of chemical dissolved in the water column is given by:

$$R_{s/w} = K_{s/w} (M_s/M_w) \quad (A-12)$$

where

R = ratio of the mass of chemical adsorbed to suspended and bottom sediment to the mass of chemical dissolved in the water column

$K_{s/w}$ = sediment/water equilibrium partition coefficient

M_s = mass of suspended sediment and exposed bottom sediment

M_w = mass of water

In most aquatic systems, M_s/M_w appears to be $<10^{-3}$ (USGS 1983). Therefore, in such systems, $K_{s/w}$ would have to be $>10^2$ for $R_{s/w}$ to be $>10^{-1}$.

As previously mentioned, the soil/water equilibrium partition coefficient can be used to qualitatively predict the susceptibility of a compound to leaching from the soil. The following equation can be used to estimate R_f values for the soil thin layer chromatography (TLC) of organics (Hamaker in Hague and Freed 1975):

$$R_f = [1 + K_{oc} f_{oc} d_s (1/\theta^{2/3} - 1)]^{-1} \quad (A-13)$$

where

R_f = estimated soil thin layer chromatography R_f value

K_{oc} = organic carbon normalized soil/water equilibrium partition coefficient

f_{oc} = organic carbon fraction of soil

d_s = density of soil in g/cm^3

Θ = soil pore fraction.

Based on observed correlations between soil TLC R_f values and the susceptibility of compounds to leaching from soil, Hilling and Turner (1968) as cited by Hamaker in Hague and Freed (1975) defined the following five mobility classes for the leaching of organics from a soil with $f_{oc} = 0.014$, $p = 2.5 g/cm^3$ and $\Theta = 0.5$ based upon the magnitude of the R_f value:

<u>Mobility Class</u>	<u>R_f Range</u>
1. (Very immobile)	0 - 0.99
2. (Modertely immobile)	0.1 - 0.34
3. (Intermediate mobility)	0.35 - 0.64
4. (Moderately mobile)	0.65 - 0.89
5. (Very mobile)	0.90 - 1.00

An experimental bioconcentration factor (BCF) for a given chemical and aquatic organism is equal to the steady ratio of the concentration of the chemical in the organism in μg chemical per g of tissue to the chemical concentration in aqueous solution in $\mu g/ml$ (mg/l). Bioconcentration factors generally increase with increasing lipid content for similar aquatic species. The bioconcentration factors that are estimated from the octanol/water partition coefficient and aqueous solubility are computed from equations derived from data on a number of different aquatic organisms with different lipid contents and therefore do not represent any specific organism or lipid content. However, they can be used to qualitatively predict the bioconcentration potential of aquatic organisms in general and the general potential for biomagnification in aquatic ecosystems. Stern and Walker (1978) in ASTM (1978), indicate that compounds with a BCF value below 100, between 100 and 1,000 and above 1,000 probably have low, moderate, and high bioconcentration

potentials, respectively. Since the potential for biomagnification is dependent upon the bioconcentration potential, the ranges of BCF values listed above can also be used to predict biomagnification potential.

Abiotic Degradation: Hydrolysis, Photooxidation, Photolysis

SAIC used the following equation to estimate pseudo first order hydrolysis rate constants for chemicals in water as a function of pH (Lyman et al. 1982)

$$K_H = k_A 10^{-pH} + k_N - k_B k_W 10^{pH}$$

where

k_H = pseudo first order hydrolysis rate constant in time^{-1}

k_A = second order acid catalyzed rate constant

k_N = first order rate constant for neutral hydrolysis

k_B = second order base catalyzed rate constant

$pH = \log [H^+]$

$k_W = [H^+] [OH^-]$

Values of k_A , k_N , and k_B were taken from the literature. The pH of most natural waters is within the range of 5 to 9 (Bouwer 1978; Stumm and Morgan). Therefore, for any chemical with known or estimated values of k_A , k_N , and k_B , pseudo first order hydrolysis rate constants at pHs of 5, 6, 7, 8 and 9 were estimated from equation (A-14).

SAIC used the following equation to estimate pseudo first order photo-oxidation rate constants for chemicals in shallow sunlit surface waters (Mill 1980 in Mabey et al. 1981):

$$K_{ox} = k_{1O_2} (10^{-12} M) + k_{Ro} (10^{-9} M)$$

where

K_{ox} = pseudo first order photooxidation rate constant (hr^{-1})

k_{1O_2} = second order rate constant for oxidation by sunlit oxygen ($M^{-1} \text{hr}^{-1}$)

$(10^{-12}M)$ = assumed concentration of sunlit oxygen in shallow sunlit surface waters

k_{ro} = second order rate constant for oxidation by peroxy radicals ($M^{-1}hr^{-1}$)

$(10^{-9}M)$ = assumed concentration of peroxy radicals in shallow sunlit surface waters.

Methods for estimating direct photolysis rate constants for chemicals in aqueous solution are reviewed by Lyman et al. (1982). The magnitude of the aqueous photolysis rate constant for a given chemical depends upon the intensity of solar radiation, the attenuation of solar radiation by the water body, and the magnitudes of the absorption coefficients for the chemical at wavelengths above 290 nm (Lyman et al. 1982). Due to time restrictions and a lack of sufficient data on the magnitudes of absorption coefficients at wavelengths above 290 nm, SAIC did not attempt to estimate direct photolysis rate constants.

Biodegradation

SAIC used the following equation to estimate pseudo first order rate constants for the biodegradation of organics in natural waters (Mabey et al. 1981):

$$K_B = k_{Biol} [\text{bacteria cells}] \quad (A-16)$$

where

K_B = pseudo first order biodegradation rate constant in water (hr^{-1})

k_{Biol} = second order biodegradation rate constant in water ($ml \text{ cell}^{-1} hr^{-1}$)

$[\text{bacteria cells}]$ = concentration of bacteria cells (cells/ml).

Mabey et al. (1981) divided numerous organics into five groups according to their known or estimated susceptibility to biodegradation in water and assigned an estimated aqueous second order biodegradation rate constant k_{Biol} to each of the five groups. SAIC used these estimated k_{Biol} values to compute aqueous pseudo first order rate constants from equation (A-16).

Baughman and Lassiter (1978) in Lyman et al. (1982) suggest the use of the following active bacteria concentrations (in the absence of data) to compute aqueous first order biodegradation rate constants: 10 cell/ml for oligotrophic lakes, 10^4 cells/ml for streams, and 10^5 cells/ml for ponds and eutrophic lakes, representing a range of 10/cell to 10^5 /cell for natural surface waters. McCabe et al. (1970) in Bouver (1978) reported 17 percent of the groundwater samples from 621 wells had aerobic bacteria plate counts of 0/ml, 60 percent had counts between 1/ml and 100/ml and 7 percent had counts exceeding 1,000/ml, representing a non-zero range of 1 cell/ml to > 1,000 cells/ml. SAIC assumed the range of active bacteria concentrations in surface waters and groundwaters was 10 cell/ml to 10^5 cell/ml, and 1 cell/ml to 10^3 cell/ml, respectively for computational purposes.